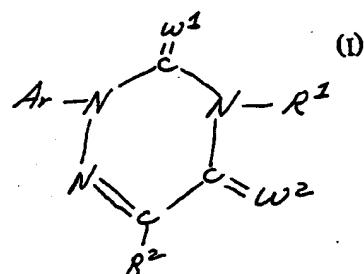




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(54) Title: HERBICIDAL 2-ARYL-1,2,4-TRIAZINE-3,5(2H,4H)-DIONES AND SULFUR ANALOGS THEREOF



(57) Abstract

Herbicidal 2-aryl-1,2,4-triazine-3,5(2H,4H)-Diones and analogous thiones, where W¹ and W² are oxygen or sulfur; R¹ is amino, alkenyl, alkynyl, alkyl or substituted alkyl; R² is hydrogen, alkenyl, alkynyl, amino, alkyl, substituted alkyl, halo, carboxyl or alkoxy carbonyl.

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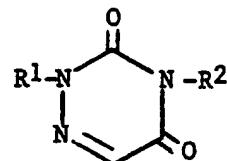
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HERBICIDAL 2-ARYL-1,2,4-TRIAZINE-3,5(2H,4H)-DIONES
AND SULFUR ANALOGS THEREOF

The invention described in this application pertains to weed control in agriculture, horticulture, and other fields where there is a desire to control unwanted plant growth. More specifically, the present application describes herbicidal 2-aryl-1,2,4-triazine-3,5(2H,4H)-diones, sulfur analogs thereof, compositions of them, methods of preparing them, and methods for preventing or destroying undesired plant growth by preemergence or postemergence application of the herbicidal compositions to the locus where control is desired. The present compounds may be used to effectively control a variety of both grassy and broadleaf plant species. The present invention is particularly useful in agriculture, as a number of the compounds described herein show a selectivity favorable to soybean, corn, cotton, wheat, rice, or other crops at application levels which prevent the growth of or destroy a variety of weeds.

1,2,4-Triazine-3,5(2H,4H)-diones as a class are generally associated with the pharmaceutical or animal health arts and are commonly referred to therein as 6-azauracils. Such compounds, however, are relatively unknown in the herbicide art. In particular, there does not appear to be any disclosure of 2-aryltriazinediones in the art. Herbicidal activity is disclosed in German Offenlegungsschrift No. 3,016,304 for optionally substituted triazine-diones having the formula

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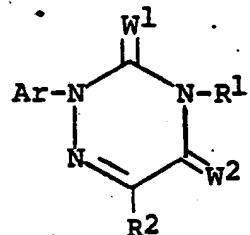
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where R¹ is hydrogen, hydroxymethyl or an ester derivative thereof such as a benzoic acid ester, optionally substituted aminomethyl, optionally halo-substituted 2-tetrahydrofuryl, 2-(2H,5H)dihydro-5 furanyl, or 2-tetrahydropyranyl, and R² is hydrogen, an optionally substituted aminomethyl, optionally halo-substituted 2-tetrahydrofuryl, or 2-tetrahydropyranyl, with certain provisos.

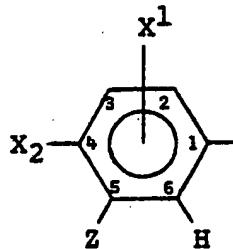
It has now been discovered that 2-aryl-1,2,4-triazine-3,5-(2H,4H)-diones and the corresponding sulfur analogs have herbicidal properties and may be used effectively either preemergently or postemergently for herbicidal purposes.

The herbicidal compounds of this invention have 15 the formula

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where Ar is an aryl radical, preferably a ring-substituted aryl radical. For instance it may have a benzene ring such as the radical indicated by the following formula

- 3 -

wherein X¹ may be for instance hydrogen or halogen, preferably fluorine or chlorine, the halogen atom advantageously being positioned at the C-2 carbon atom of the phenyl ring;

5 X² may be hydrogen, halogen such as fluorine, chlorine, or bromine, alkyl of 1 to 6 (preferably 1 to 4) carbon atoms, particularly methyl, haloalkyl of 1 to 5 carbon atoms, for example, trifluoromethyl, alkoxy of 1 to 6 (preferably 1 to 4) carbon atoms, or 10 phenoxy or phenylmethoxy which may be ring substituted with halogen or alkyl or alkoxy of 1 to 4 carbon atoms;

Z may be hydrogen or, preferably, a substituent or group selected from fluorine, chlorine, bromine, 15 iodine, cyano, nitro, amino, alkoxycarbonylamino of 1 to 6 (preferably 1 to 4) alkyl carbon atoms, di-(alkylcarbonyl)amino in which each alkyl is of 1 to 6 (preferably 1 to 4) carbon atoms, hydroxysulfonyl, alkyl of 1 to 6 (preferably 1 to 4) carbon atoms, 20 haloalkyl of 1 to 5 carbon atoms, -QR, -CO-R⁶, -S(O)_mR⁸, -Q²R⁹, -OSO₂R¹⁰, -NHN=CR¹¹R¹², and -Q-CR³R⁴-(CH₂)_n-CO-Q¹-R⁵.

For Z = -QR, Q may be O, S, or NR⁷; R⁷ may be 25 hydrogen or alkyl of 1 to 6 (preferably 1 to 4) carbon atoms; and R may be alkyl of 1 to 6 (preferably 1 to 4) carbon atoms which may be substituted with cycloalkyl of 3 to 7 carbon atoms (for example, methyl, 1-methylethyl, or cyclohexylmethyl), cycloalkyl of 3 to 7 (preferably 5 or 6) carbon atoms which may be 30 substituted with alkyl of 1 to 6 carbon atoms (for example, cyclopentyl or methylcyclopropyl), alkoxyalkyl of 2 to 8 (preferably 2 to 4) carbon atoms (for example, ethoxymethyl), alkoxyalkoxyalkyl of 3 to 8 (preferably 3 to 5) carbon atoms (for example, 2-methoxyethoxymethyl), alkylthioalkyl of 2 to 8 (preferably 2 to 4) carbon atoms or the sulfinyl or sulfonyl derivative thereof, tri(alkyl of 1 to 4 carbon atoms)-

silyl(alkyl of 1 to 4 carbon atoms) such as trimethylsilylmethyl, cyanoalkyl of 1 to 5 (preferably 1 to 3) alkyl carbon atoms such as cyanomethyl or 2-cyanoethyl, alkenyl of 2 to 5 (preferably 3 to 5) carbon atoms such as 2-propenyl, alkynyl of 2 to 5 (preferably 3 to 5) carbon atoms such as 2-propynyl, haloalkyl of 1 to 5 (preferably 1 to 3) carbon atoms especially a fluoroalkyl, haloalkenyl of 2 to 5 (preferably 3 to 5) carbon atoms, haloalkynyl of 2 to 5 (preferably 3 to 5) carbon atoms such as 3-bromo-2-propynyl, alkylcarbonyl of 1 to 6 (preferably 1 to 4) alkyl carbon atoms such as acetyl, or dialkylamino-carbonyl or dialkylaminothiocarbonyl in which each alkyl is of 1 to 6 (preferably 1 to 4) carbon atoms.

15 The compounds in which $Z = -QR$, especially where X^1 is 2-F and X^2 is Cl or Br, form a preferred embodiment of the invention; particularly where Q is sulfur, more particularly where Q is oxygen. Frequently, R will be selected from among alkyl, cyanoalkyl, alkynyl, haloalkynyl, and alkoxyalkyl. Typical such R groups include, for example, 1-methylethyl, cyanomethyl, 2-propynyl, 3-bromo-2-propynyl, and methoxymethyl. Preferably R will be 1-methylethyl or, especially, 2-propynyl or methoxymethyl.

20 For $Z = -CO-R^6$, R^6 may be hydroxy, alkoxy or alkylthio of 1 to 6 (preferably 1 to 4) carbon atoms such as methoxy or methylthio, alkoxyalkoxy of 2 to 6 (preferably 2 to 4) carbon atoms (for example, 2-methoxyethoxy), amino, or alkylamino or dialkylamino wherein each alkyl is of 1 to 6 (preferably 1 to 4) carbon atoms and may be substituted with alkoxy of 1 to 4 carbon atoms (for example, methylamino, dimethylamino, or methyl(2-methoxyethyl)amino). For example, Z, defined as $-CO-R^6$, may be CO_2H , CO_2 alkyl,

25 $CO-S$ -alkyl, CO_2 alkyl-O-alkyl, $CONH_2$, or $CONH$ -alkyl or $CON(alkyl)_2$ in which any alkyl may be substituted with alkoxy. Compounds in which Z is $-CO-R^6$,

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especially where X^1 is 2-F and X^2 is Cl or Br, form a preferred embodiment of the invention.

For $Z = -S(O)_{\bar{m}} R^8$, m may be 1 or 2 and R^8 may be alkyl of 1 to 6 (preferably 1 to 4) carbon atoms or 5 alkenyl or alkynyl of 2 to 5 (preferably 3 to 5) carbon atoms. For example, Z may be $-SO_2CH_3$, $-SO_2CH(CH_3)_2$, $-SO_2CH_2CH=CH_2$, or $-SO_2CH_2C\equiv CH$.

For $Z = -Q^2R^9$, Q^2 may be sulfur or, preferably, oxygen, and R^9 may be a 5- or 6-membered ring 10 heterocyclic group of 1 or 2 same or different (preferably the same) heteroatoms selected from O, S (including the S-oxide and S-dioxide), and N or an alkyl radical of 1 to 5 (preferably 1 to 3) carbon atoms substituted with said heterocyclic group. R^9 15 will frequently be

(a) an optionally substituted and optionally benzene-adjoined nitrogen-containing heterocycle or an alkyl radical of 1 to 5 carbon atoms substituted with said heterocycle;

20 (b) an aromatic, optionally substituted and optionally benzene-adjoined, oxygen- or sulfur-containing heterocycle or an alkyl group of 1 to 5 carbon atoms substituted therewith; or, advantageously,

25 (c) a non-aromatic, optionally substituted and optionally benzene-adjoined, oxygen- or sulfur-containing heterocycle or an alkyl group of 1 to 5 carbon atoms substituted therewith.

Examples of R^9 groups include 1-methyl-3-pyrrolidinyl, furfuryl, 2-thienylmethyl, 3-tetrahydrofuran-2-yl, tetrahydrofurfuryl, tetrahydropyran-2-ylmethyl, 1,3-dioxolan-2-ylmethyl, 2-(1,3-dioxolan-2-yl)ethyl, 2,2-dimethyl-1,3-dioxolan-4-ylmethyl, 3-(2-methyl-1,3-dioxolan-2-yl)propyl, 1,3-dioxan-4-ylmethyl, 1,4-benzodioxan-2-ylmethyl, tetrahydro-4H-pyran-4-yl, 5,6-dihydro-2H-pyran-3-ylmethyl, 2,2-dimethyl-1,3-dithiolan-4-ylmethyl, tetrahydro-4H-

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thiopyran-4-yl, tetrahydrothien-3-yl, 1-oxotetrahydrothien-3-yl, 1,1-dioxotetrahydrothien-3-yl, 2,2-dimethyl-1,1,3,3-tetraoxo-1,3-dithiolan-4-yl-methyl, 1,1-dioxotetrahydro-4H-thiopyran-4-yl, and
 5 1,3-oxothiolan-2-ylmethyl.

For Z = $-\text{OSO}_2\text{R}^{10}$, R¹⁰ may be alkyl of 1 to 6 (preferably 1 to 4) carbon atoms (which may be substituted with halogen, cyano, alkoxy or alkylthio of 1 to 4 carbon atoms, or alkylamino or dialkylamino in which alkyl is of 1 to 4 carbon atoms), phenyl, or alkyl-amino or dialkylamino in which alkyl is of 1 to 4 carbon atoms. Examples of such Z substituents include phenylsulfonyloxy, methysulfonyloxy, ethylsulfonyloxy, propylsulfonyloxy, butylsulfonyloxy, 1-methyl-15 ethylsulfonyloxy, 1-methylpropylsulfonyloxy, 2-methyl-propylsulfonyloxy, 3-methylbutylsulfonyloxy, chloromethylsulfonyloxy, 3-chloropropylsulfonyloxy, trifluoromethylsulfonyloxy, methylaminosulfonyloxy, dimethylaminosulfonyloxy, dimethylaminoethylsulfonyloxy,
 20 2-methoxyethylsulfonyloxy, 2-ethoxyethylsulfonyloxy, and cyanomethylsulfonyloxy.

For Z = $-\text{NHN}=\text{C}(\text{R}^{11})(\text{R}^{12})$, one of R¹¹ and R¹² may be hydrogen or alkyl of 1 to 4 carbon atoms and the other may be alkyl of 1 to 4 carbon atoms, or 25 C(R¹¹)(R¹²) taken as a unit may be cycloalkyl of 3 to 7 (preferably 5 to 7) carbon atoms. For example, Z may be NHN=C(CH₃)₂, NHN=CHCH₂CH₃, NHN=C(CH₃)(C₂H₅), NHN=C(CH₂)₃CH, or NHN=C(CH₂)₄CH.

30 For Z = $-\text{Q}-\overset{\text{R}^3}{\underset{\text{R}^4}{\text{C}}}-(\text{CH}_2)_n-\text{CO-Q}^1-\text{R}^5$, n may be 0 to 2, preferably 0; R³ may be hydrogen or alkyl of 1 to 4 carbon atoms; R⁴ may be hydrogen, alkyl of 1 to 4 carbon atoms, or alkoxy of 1 to 4 carbon atoms; Q and Q¹ may be independently O, S, or NR⁷ in which R⁷ is hydrogen or alkyl of 1 to 6 (preferably 1 to 4) carbon atoms; and R⁵ may be hydrogen, alkyl of 1 to 6

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(preferably 1 to 4) carbon atoms which may be substituted with cycloalkyl of 3 to 7 carbon atoms (for example, methyl, cyclopropylmethyl, cyclopentylmethyl, or cyclohexylmethyl), cycloalkyl of 3 to 7 carbon atoms 5 which may be substituted with alkyl of 1 to 4 carbon atoms (for example, methylcyclopropyl, cyclopentyl, cyclohexyl, 2-methylcyclohexyl, or cycloheptyl), alkoxyalkyl or alkylthioalkyl of 2 to 6 carbon atoms, haloalkyl of 1 to 5 carbon atoms (especially fluoro- 10 alkyl or chloroalkyl), alkenyl of 2 to 5 carbon atoms such as 2-propenyl, cycloalkenyl of 5 to 7 carbon atoms which may be substituted with alkyl of 1 to 4 carbon atoms (for example, 2-cyclohexenyl), cycloalkenylalkyl of 6 to 10 carbon atoms (for example, 3-cyclohexenyl- 15 methyl), phenyl or phenylmethyl (each of which may be ring-substituted with fluorine, chlorine, bromine, or alkyl, alkoxy, or alkylthio of 1 to 4 carbon atoms), cyanoalkyl of 1 to 5 alkyl carbon atoms such as cyano- methyl, alkynyl of 2 to 5 carbon atoms such as 2-pro- 20 pynyl, alkylimino of 1 to 6 (preferably 1 to 4) carbon atoms which may be substituted with cycloalkyl of 3 to 7 carbon atoms, or cycloalkylimino of 5 to 7 carbon atoms which may be substituted with alkyl of 1 to 4 carbon atoms; or Q¹ and R⁵ may together represent a 25 phenylsulfonylamino group in which the phenyl is unsubstituted or substituted with halogen such as fluorine, chlorine, or bromine, alkyl of 1 to 4 carbon atoms, alkoxy of 1 to 4 carbon atoms, or alkoxycarbonyl of 1 to 4 alkyl carbon atoms.

30 This subgenus, especially where X¹ is 2-F and X² is Cl or Br, forms a preferred embodiment of the invention; particularly where n is 0 and one of R³ and R⁴ is H and the other is H, CH₃, C₂H₅, OCH₃, or OC₂H₅. Where Q or Q¹ is NR⁷, R⁷ is preferably H. 35 Examples of Z substituents where Q is NR⁷ include those of the formulas -NHCH₂CO₂R⁵ and -NHCH(CH₃)CO₂R⁵

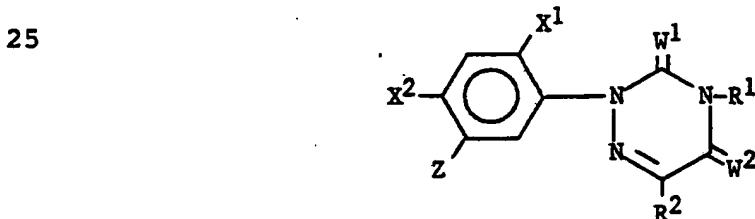
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where R⁵ is methyl, ethyl, propyl, butyl, 2-methoxyethyl, 2-propoxyethyl, 2-cyanoethyl, 2,3-dichloropropyl, 2,2-dichloroethyl, cyclopentylmethyl, cyclopentyl, 1-methylethyl, 1-ethylpropyl, or 1-methylpropyl.

- 5 Thus, Z may be H or a substituent or group such as F, Cl, Br, I, NO₂, NH₂, CN, SO₃H, alkyl, haloalkyl, OR, SR, NR⁷R, NHCO₂-alkyl, N(CO-alkyl)₂, CO-R⁶, SO-R⁸, SO₂-R⁸, OR⁹, SR⁹, OSO₂R¹⁰, NHN=CR¹¹R¹², O-CR³R⁴-CO₂R⁵, O-CR³R⁴-CO-SR⁵, O-CR³R⁴-CO-NR⁷R⁵, S-CR³R⁴-CO₂R⁵,
10 S-CR³R⁴-CO-SR⁵, S-CR³R⁴-CO-NR⁷R⁵, NR⁷-CR³R⁴-CO₂R⁵, NR⁷-CR³R⁴-CO-SR⁵, or NR⁷-CR³R⁴-CO-NR⁷R⁵.

- The aryl moiety of the present aryltriazinediones may be a heteroaromatic radical such as a furyl, thienyl, pyridyl, pyrimidyl, oxazolyl, pyrrolyl, 15 isoxazolyl, thiazolyl, or isothiazolyl radical which may carry one or more substituents, for example, halogen and/or alkyl or alkoxy of 1 to 6 (preferably 1 to 4) carbon atoms. Preferably, however, the aryl moiety will be a phenyl radical, particularly a 20 halophenyl radical, more particularly a dihalophenyl radical.

In a preferred embodiment for herbicidal activity, the present compounds will have the formula:



- 30 in which X¹ and X² are both halogen atoms and Z is as defined above. X¹ is preferably chlorine or, especially, fluorine. X² is preferably chlorine or bromine.

- 35 With respect to the triazinedione portion of the molecule, R¹ may be alkyl of 1 to 6 (preferably 1 to 4) carbon atoms; haloalkyl of 1 to 5 (preferably 1 to

3) carbon atoms; cyanoalkyl of 1 to 5 (preferably 1 to 3) alkyl carbon atoms; alkenyl or alkynyl of 2 to 5 (preferably 3 to 5) carbon atoms; alkoxyalkyl, alkyl-thioalkyl, alkylsulfinylalkyl, or alkylsulfonylalkyl of 5 2 to 5 (preferably 2 to 4) carbon atoms; or amino.

R¹ will frequently and conveniently be a lower alkyl group such as methyl or ethyl, especially methyl. When R¹ is haloalkyl, the alkyl radical may be substituted with one or more same or different halogen atoms, preferably the same and preferably fluorine. Typical fluoroalkyl groups include fluoromethyl, difluoromethyl, 2-fluoroethyl, and 3-fluoropropyl. Examples of other R¹ substituents include cyanomethyl, amino, 10 2-propenyl, 2-propynyl, 2-methoxyethyl, methylthiomethyl, methylsulfinylmethyl, and methylsulfonylmethyl. In a preferred embodiment, R¹ is methyl or a fluoromethyl having 1 or 2 fluorine atoms, especially methyl.

R² may be hydrogen; halogen, especially fluorine, 20 chlorine, or bromine; alkyl of 1 to 4 carbon atoms, especially methyl; haloalkyl of 1 to 4 carbon atoms, particularly a fluoroalkyl such as trifluoromethyl; cyanoalkyl of 1 to 4 alkyl carbon atoms such as cyanomethyl; alkenyl of 2 to 4 carbon atoms such as 2-propenyl; alkynyl of 2 to 4 carbon atoms such as 2-propynyl; alkoxyalkyl of 2 to 4 carbon atoms, for example, 2-methoxyethyl; amino; hydroxycarbonyl; or alkoxy carbonyl of 1 to 4 alkyl carbon atoms. Compounds in which R² is hydroxycarbonyl, while in themselves or as salts are generally herbicidal at high application 25 rates, are more useful as intermediates (for the corresponding compounds in which R² is hydrogen) than as herbicides. In a preferred embodiment, R² is hydrogen or methyl, especially hydrogen.

30 35 The groups W¹ and W² are independently selected from oxygen and sulfur. Thus, W¹ and W² may both be oxygen or sulfur, W¹ may be oxygen and W² may be

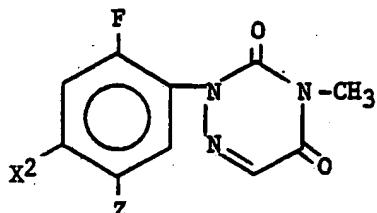
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sulfur, or W^1 may be sulfur and W^2 may be oxygen. In a preferred embodiment W^1 and W^2 are both oxygen.

A preferred subgenus for high herbicidal activity comprises the compounds of the formula

5

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Ia

in which X^2 is bromine or chlorine and Z is as defined above. Compounds in which the fluorine atom at C-2 of the phenyl ring is replaced by a chlorine atom and Z is 15 other than hydrogen are also of particular interest.

It will be understood that any alkyl, alkenyl or alkynyl group herein may be straight chain or branched chain radicals. Thus, 1-methylethyl, 2-methyl-2-propenyl, and 1-methyl-2-propynyl are branched chain 20 examples of alkyl, alkenyl, and alkynyl radicals respectively. Halogen may be fluorine, chlorine, bromine, or iodine. Haloalkyl radicals may have one or more same or different halogen atoms.

Any herbicidal compound of the present invention in 25 which R^2 is CO_2H or in which Z is or contains SO_3H or CO_2H may, of course, be converted into a salt such as a sodium, potassium, calcium, ammonium, magnesium, or mono-, di-, or tri(C_1 to C_4 alkyl)-ammonium salt which may also be used as an herbicide. 30 Such salts are within the scope of the present invention.

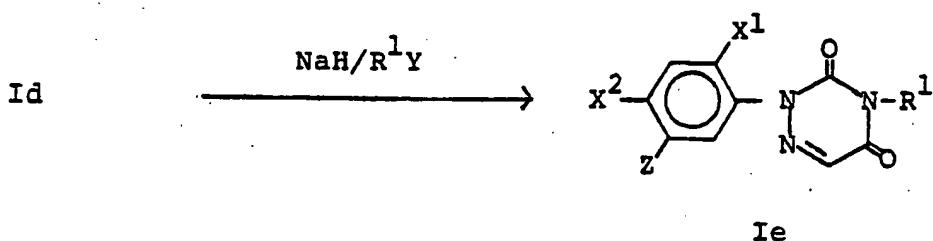
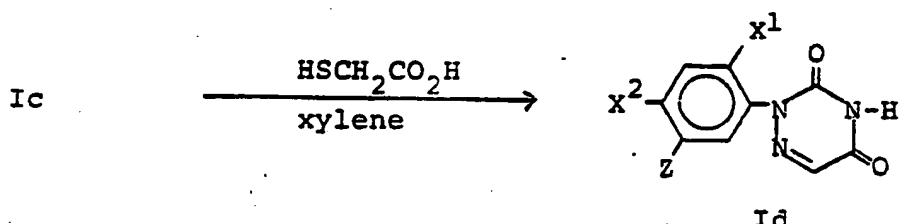
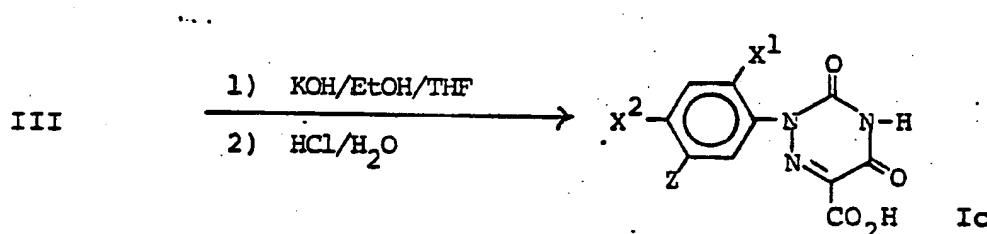
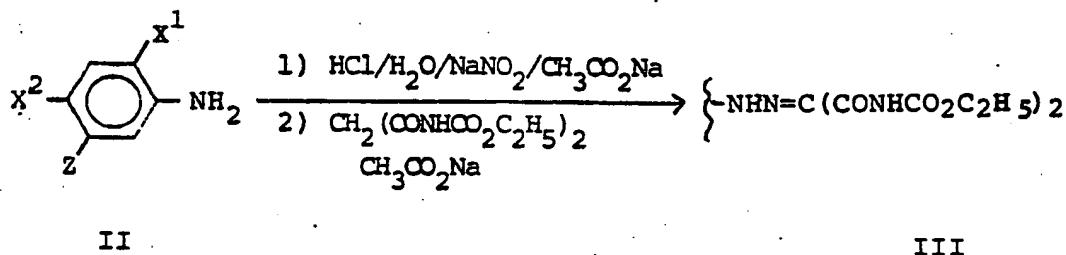
A number of the compounds of the invention may more readily exist in hydrated form rather than as non-hydrated materials. It will be understood that the 35 presence or absence of water of hydration in the compounds is of no concern in determining the metes and bounds of the present invention.

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The present compounds may be prepared by methods described in the literature or by methods analogous or similar thereto and within the skill of the art.

Many of the present compounds may be prepared as
5 illustrated in the following chemical equations:

Method A: $R^2 = H$ or CO_2H

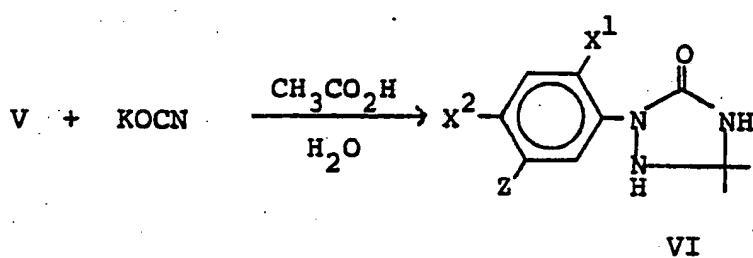
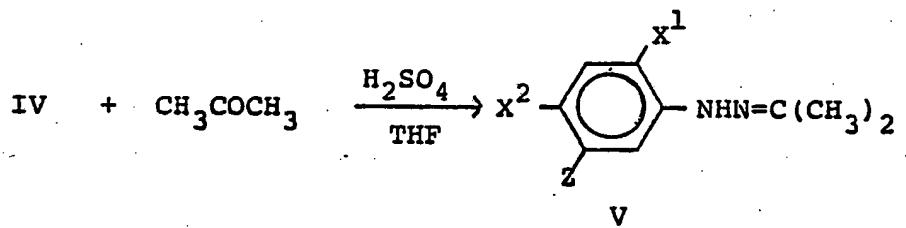
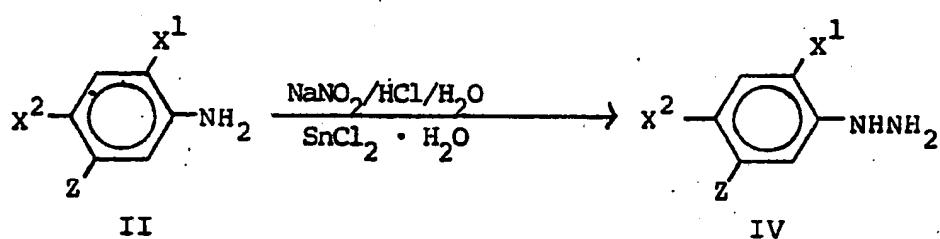


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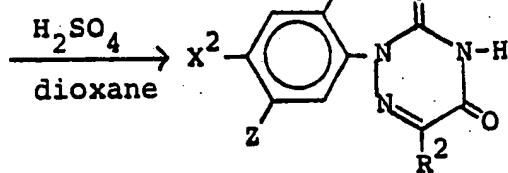
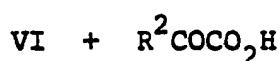
An appropriately substituted aniline, II, is treated first with aqueous hydrochloric acid, sodium acetate, and sodium nitrite, then with malonyldiurethane and sodium acetate to produce intermediate III.

- 5 Compound III is cyclized by treatment first with ethanolic potassium hydroxide in tetrahydrofuran, then with aqueous hydrochloric acid to give the triazine-dione carboxylic acid Ic which is decarboxylated in the presence of mercaptoacetic acid and xylene to give the 10 intermediate Compound Id. Treatment of Id with R¹Y, in which Y is a suitable leaving group, in the presence of a base gives the N-substituted triazinedione Ie.

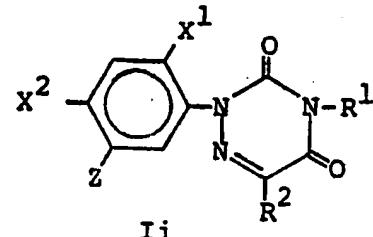
Method B: R² = H, alkyl



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Ih



II

10 An appropriately substituted aniline is reacted with sodium nitrite and tin (II) chloride in aqueous hydrochloric acid to produce the corresponding hydrazine, Compound IV, which is converted to hydrazone V by treatment with acetone in sulfuric acid and tetrahydrofuran. Treatment of V with potassium cyanate in aqueous acetic acid gives triazolidinone VI which upon reaction with $\text{R}^2\text{COCO}_2\text{H}$ and sulfuric acid in dioxane produces triazinedione Ih. Reaction of Ih with R^1Y wherein Y is a leaving group gives product II.

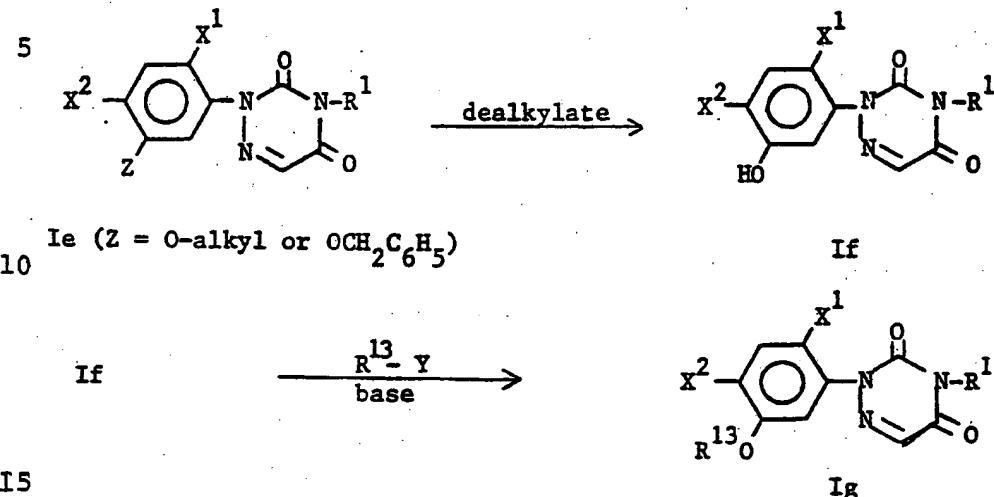
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20 The methods illustrated above for producing Ie and II are generally applicable where the starting material Compound II is readily available, either commercially or by preparation, and the substituent Z is stable under the conditions of the process. In some instances 25 the desired Z substituent may be unstable under the conditions used in preparing the starting material II or in converting II into product Ie or II. In such cases or where it is otherwise not desirable or convenient to have the desired Z substituent in place at 30 the outset, in Compound II, it may be advantageous to incorporate the desired Z group into the molecule further on in the process, for example, subsequent to the addition of the R^1 group.

For example, the products in which Z is $-\text{OR}^9$, 35 $-\text{OSO}_2\text{R}^{10}$, $-\text{OCR}^3\text{R}^4\text{CO-Q}^1\text{R}^5$, or $-\text{OR}$ (R is other than

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lower alkyl) may advantageously be prepared from Compound Ie (or II) in which Z is lower alkoxy or benzyloxy as illustrated in the following chemical equations:

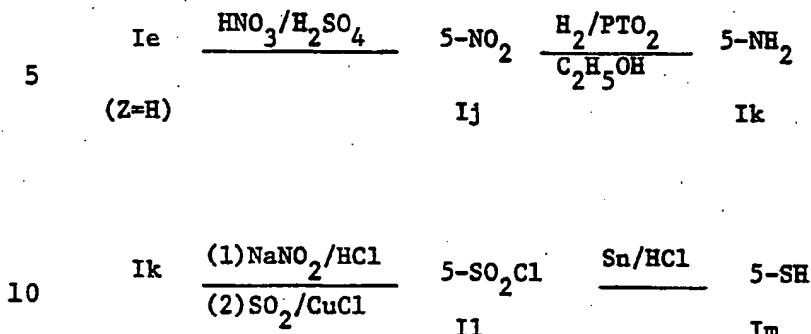


In the equations above R¹³ represents the appropriate radical -R⁹, -SO₂R¹⁰, -CR³R⁴-CO-Q¹R⁵, or -R and Y represents a leaving group. The phenolic intermediate If is readily prepared from the corresponding compound Ie in which Z is lower alkoxy or benzyloxy by treatment with an acidic reagent such as concentrated sulfuric acid, concentrated hydrobromic acid, or a mixture of hydrobromic and acetic acids to effect dealkylation, or, where Z is benzyloxy, by hydrogenolysis over palladium on charcoal (H₂/Pd/C/C₂H₅OH). Reaction of the 5-hydroxyphenyl intermediate If with the appropriate R⁹-Y, R¹⁰-SO₂Y, Y-CR³R⁴-CO-Q¹R⁵, or R-Y, i.e., R¹³-Y in the equation above, in the presence of a base gives product Ig.

Similarly, products corresponding to Ie or II in which Z is -SR¹³, where R¹³ has the meaning given above, may be prepared by treatment of the corresponding 5-mercaptophenyl compound with R¹³-Y. The 5-mercaptophenyl compound may be prepared from the corresponding compound in which Z is hydrogen (Ie or

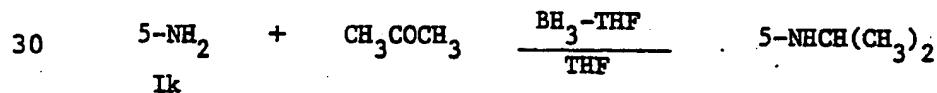
- 15 -

Ii, Z = H) by the sequence of steps illustrated below:



Compound Ie in which Z is hydrogen may be nitrated to give the corresponding 5-nitro compound Ij, which may be reduced to give the corresponding 5-amino compound 15 Ik. Compound Ik may be treated first with NaNO_2/HCl , then with SO_2/CuCl to give the 5-chlorosulfonyl compound Ii which may be reduced with Sn/HCl to give the corresponding 5-mercaptop compound Im.

As with the 5-OH and 5-SH intermediates, the 20 5-NH₂ compound, Ik, is an important intermediate which may be alkylated or acylated to introduce other Z substituents into the molecule. Compounds in which Z is alkoxy carbonylamino, di(alkylcarbonyl)amino, -NR⁷R, or -NR⁷-CR³R⁴-CO-Q¹R⁵ may be prepared in 25 this manner from the corresponding 5-NH₂ compound. An alternative method for introducing certain -NHR or -NH-CR³R⁴-CO-Q¹R⁵ Z groups is illustrated in the equation below:



For example, Compounds 89 (Z = -NHCH(CH₃)₂), 206 (Z = -NH-cyclohexyl), and 232 (Z = -NH-CH(CH₃)-CO₂C₂H₅) shown in Table 1 below were prepared by condensing the 35 corresponding 5-NH₂ compound with the appropriate ketone in the presence of borane in tetrahydrofuran.

The compound of formula Ie or II in which Z is

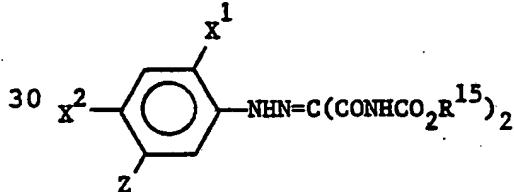
- 16 -

-NHN=CR¹¹R¹² may also be produced from the corresponding compound in which Z is -NH₂ by reacting the 5-NH₂ compound with NaNO₂ and SnCl₂ in aqueous HCl to give the corresponding hydrazine (Ie, Z = -NHNH₂), 5 followed by condensation with R¹¹COR¹².

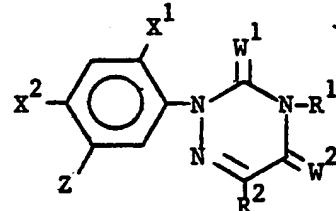
The amino compounds (Ie or II, Z = -NH₂) may also be converted into the corresponding compounds in which Z is a halogen atom by treatment with nitrous acid under conditions which give a diazonium salt followed 10 by treatment of the salt with the appropriate halogen reagent, for example, CuCl, CuBr, KI, or HBF₄.

The compounds of formula I in which W¹ or W² or both are sulfur may be prepared as follows. Compound Ie or II may be treated with one equivalent of P₂S₅ 15 in pyridine to give the corresponding compound of formula I in which W² is sulfur; or Ie or II may be treated with at least two equivalents of P₂S₅ to produce the dithione derivative (I, W¹ = W² = S). Compound I in which W¹ is sulfur and W² is oxygen 20 may be prepared by substituting KSCN for KO CN in Method B above to produce the triazolidinethione corresponding to the triazolidinone VI which may then be carried through the Method B process to give the 1,2,4-triazine-3-thione-5-one product.

25 The novel intermediates for the present herbicidal compounds are also part of the present invention, particularly compounds VII, VIII, IX, and X.



VII



VIII (R¹=H)
IX (R¹=CO₂H)
X (Z=OH, SH, or NH₂)

In each of the compounds above, X^1 , X^2 , W^1 , and W^2 are as defined above. Preferably X^1 and X^2 are both halogen, especially fluorine, chlorine, or bromine. In a particularly preferred embodiment, 5 X^1 is chlorine or, especially, fluorine and X^2 is chlorine or bromine. W^1 and W^2 are preferably both oxygen.

For compound VII, R^{15} is an alkyl group, preferably of 1 to 4 carbon atoms, which may be substituted 10 or unsubstituted, and:

Z is fluorine, chlorine, bromine, iodine, cyano, nitro, amino, alkoxy carbonyl amino of 1 to 6 alkyl carbon atoms, di(alkyl carbonyl) amino in which each alkyl is of 1 to 6 carbon atoms, hydroxysulfonyl, halo-15 sulfonyl, alkyl of 1 to 6 carbon atoms, haloalkyl of 1 to 5 carbon atoms, $-QR$, $-CO-R^6$, $-S(O)_mR^8$, $-Q^2R^9$, $-OSO_2R^{10}$, $NHN=CR^{11}R^{12}$, or $-Q-CR^3R^4-CO-Q^1-R^5$; Q and Q^1 are independently O, S, or NR^7 in which R^7 is hydrogen or alkyl of 1 to 6 carbon atoms; 20 Q^2 is O or S;

R is hydrogen, alkyl of 1 to 6 carbon atoms (which is unsubstituted or substituted with cycloalkyl of 3 to 7 carbon atoms), cycloalkyl of 3 to 7 carbon atoms (which is unsubstituted or substituted with alkyl of 1 25 to 6 carbon atoms), benzyl, alkoxyalkyl of 2 to 8 carbon atoms, alkoxyalkoxyalkyl of 3 to 8 carbon atoms, alkylthioalkyl, alkylsulfinylalkyl, or alkylsulfonylalkyl of 2 to 8 carbon atoms, tri(alkyl of 1 to 4 carbon atoms)silyl(alkyl of 1 to 4 carbon atoms), cyano-30 alkyl of 1 to 5 alkyl carbon atoms, alkenyl or haloalkenyl of 2 to 5 carbon atoms, alkynyl or haloalkynyl of 2 to 5 carbon atoms, haloalkyl of 1 to 5 carbon atoms, alkylcarbonyl of 1 to 6 alkyl carbon atoms, or dialkylaminocarbonyl or dialkylaminothiocarbonyl in 35 which each alkyl is of 1 to 6 carbon atoms;

R^3 is hydrogen or alkyl of 1 to 4 carbon atoms, and R^4 is hydrogen, alkyl of 1 to 4 carbon atoms, or

alkoxy of 1 to 4 carbon atoms;

R^5 is hydrogen, alkyl of 1 to 6 carbon atoms

(which is unsubstituted or substituted with cycloalkyl of 3 to 7 carbon atoms), cycloalkyl of 3 to 7 carbon

5 atoms (which is unsubstituted or substituted with alkyl of 1 to 4 carbon atoms), alkoxyalkyl or alkylthioalkyl of 2 to 6 carbon atoms, haloalkyl of 1 to 5 carbon

atoms, alkenyl of 2 to 5 carbon atoms, cycloalkenyl of 5 to 7 carbon atoms (which is unsubstituted or substi-

10 tuted with alkyl of 1 to 4 carbon atoms), cycloalkenyl-alkyl of 6 to 10 carbon atoms, phenyl or phenylmethyl (each of which is unsubstituted or ring-substituted

with fluorine, chlorine, bromine, or alkyl, alkoxy or alkylthio of 1 to 4 carbon atoms), cyanoalkyl of 1 to 5

15 alkyl carbon atoms, alkynyl of 2 to 5 carbon atoms, alkylimino of 1 to 6 carbon atoms (which is unsubsti-

tuted or substituted with cycloalkyl of 3 to 7 carbon atoms), or cycloalkylimino of 5 to 7 carbon atoms

(which is unsubstituted or substituted with alkyl of 1

20 to 4 carbon atoms); or Q^1 and R^5 together represent

a phenylsulfonylamino group in which the phenyl is unsubstituted or substituted with fluorine, chlorine, bromine, alkyl of 1 to 4 carbon atoms, alkoxy of 1 to 4 carbon atoms, or alkoxycarbonyl of 1 to 4 alkyl carbon

25 atoms;

R^6 is hydroxy, alkoxy or alkylthio of 1 to 6 carbon atoms, alkoxyalkoxy of 2 to 6 carbon atoms, amino, or alkylamino or dialkylamino wherein each alkyl is of 1 to 6 carbon atoms and is unsubstituted or substituted with alkoxy of 1 to 4 carbon atoms;

R^8 is alkyl of 1 to 6 carbon atoms or alkenyl or alkynyl of 2 to 5 carbon atoms and m is 1 or 2;

R^9 is a 5- or 6-membered ring heterocyclic group of 1 or 2 same or different heteroatoms selected from 35 O, S, and N or an alkyl radical of 1 to 5 carbon atoms substituted with said heterocyclic group;

R^{10} is alkyl of 1 to 6 carbon atoms (which is

unsubstituted or substituted with halogen, cyano, alkoxy or alkylthio of 1 to 4 carbon atoms, or alkyl-amino or dialkylamino in which alkyl is of 1 to 4 carbon atoms), phenyl, or alkylamino or dialkylamino in which alkyl is of 1 to 4 carbon atoms; and

R¹¹ is hydrogen or alkyl of 1 to 4 carbon atoms and R¹² is alkyl of 1 to 4 carbon atoms, or C(R¹¹)(R¹²) taken as a unit is cycloalkyl of 3 to 7 carbon atoms.

10 Preferably Z is fluorine, chlorine, bromine, iodine, cyano, nitro, amino, hydroxysulfonyl, chlorosulfonyl, or a group -OR in which R is alkyl of 1 to 6 carbon atoms, benzyl, alkoxyalkyl of 2 to 4 carbon atoms, or alkenyl or alkynyl of 2 to 5 carbon atoms.

15 In a particularly preferred embodiment Z is -OR in which R is alkyl of 1 to 4 carbon atoms or benzyl.

For compound VIII (R¹ = H), Z is as defined above for compound VII and R² is hydrogen, hydroxycarbonyl, or alkyl of 1 to 4 carbon atoms such as methyl. R² is preferably hydrogen or hydroxycarbonyl.

For compound IX (R² = CO₂H), Z is as defined above for compound VII and R¹ is alkyl of 1 to 6 carbon atoms, haloalkyl of 1 to 5 carbon atoms, cyanoalkyl of 1 to 5 alkyl carbon atoms, alkenyl or alkynyl of 2 to 5 carbon atoms, alkoxyalkyl, alkylthioalkyl, alkylsulfinylalkyl, or alkylsulfonylalkyl of 2 to 5 carbon atoms. R¹ is preferably alkyl of 1 to 4 carbon atoms, cyanoalkyl of 1 to 3 alkyl carbon atoms, fluoroalkyl of 1 to 3 carbon atoms, alkenyl or alkynyl of 3 to 5 carbon atoms, alkoxyalkyl of 2 to 4 carbon atoms, alkylthioalkyl of 2 to 4 carbon atoms, alkylsulfinylalkyl of 2 to 4 carbon atoms, or alkylsulfonylalkyl of 2 to 4 carbon atoms. For example, R¹ may be methyl, ethyl, cyanomethyl, 2-propenyl, 2-propynyl, fluoromethyl having 1 or 2 fluorine atoms, 2-fluoroethyl, 3-fluoropropyl, methoxymethyl, methylthiomethyl, methylsulfinylmethyl, or methylsulfonyl-

methyl, especially methyl.

For compound X ($Z = OH$, SH , or NH_2), R^1 is as defined above for compound IX and R^2 is hydrogen or alkyl of 1 to 4 carbon atoms such as methyl, R^2 is preferably hydrogen.

Representative compounds of the invention are shown in Table 1. Characterizing data for many of the compounds are given in Table 2.

The preparation and herbicidal activity of representative compounds of this invention are illustrated further in the examples below. All temperatures are in degrees Celsius, and all pressures are in mm Hg.

EXAMPLE I

15 2-(2,4-DICHLOROPHENYL)-4,6-DIMETHYL-1,2,4-TRIAZINE-
3,5-(2H,4H)-DIONE

Step A 2-(2,4-Dichlorophenyl)-6-methyl-
 1,2,4-triazine-3,5(2H,4H)-dione

To a stirred solution of 4.32 g (0.020 mole) of 2,4-di-chlorophenylhydrazine hydrochloride in 100 mL of water and 50 mL of ethanol was added dropwise 2.14 g (0.024 mole) of pyruvic acid in 50 mL of water. Upon complete addition, a precipitate formed and was collected by filtration and dried under reduced pressure at ambient temperature. The solid hydrazone product was dissolved in 100 mL of toluene to which 4.8 g (0.041 mole) of thionyl chloride was added. The resultant mixture was stirred and heated at reflux for 0.5 hour. Distillation of the solvent under reduced pressure left a solid residue, which was dissolved in 100 mL of toluene. Urethane (2.2 g, 0.024 mole) was added, and the resultant solution heated at reflux with stirring for two hours. The solvent was removed from the mixture by distillation under reduced pressure to leave a residue. This residue was subjected to column chromato-

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graphy on silica gel, eluting with ethyl acetate:heptane (1:1). Appropriate fractions were combined, and the solvent removed by evaporation to leave a gummy residue. The residue was dissolved in 75 mL of ethanol 5 and 75 mL of 1N sodium hydroxide. The resultant solution was heated to 60°C, then poured into a mixture of 3N hydrochloric acid and ice. A solid formed which was collected by filtration and dried under reduced pressure. Recrystallization from tetrahydrofuran:heptane 10 provided 2.0 g of 2-(2,4-dichlorophenyl)-6-methyl-1,2,4-triazine-3,5(2H,4H)-dione (mp 197°C dec), Compound 4 in the tables.

The nmr and ir spectra were consistent with the assigned structure.

15

Step B 2-(2,4-Dichlorophenyl)-4,6-dimethyl-1,2,4-triazine-3,5(2H,4H)-dione

A solution of 1.1 g (0.0040 mole) of 2-(2,4-dichlorophenyl)-6-methyl-1,2,4-triazine-3,5(2H,4H)-dione in 5 mL of N,N-dimethylformamide was added to a stirred mixture of 0.11 g (0.0045 mole) of sodium hydride in 10 mL of N,N-dimethylformamide. After 0.5 hour, 0.63 g (0.0045 mole) of iodomethane in 5 mL of N,N-dimethylformamide was added, and the resultant mixture was stirred for approximately 18 hours. The mixture was poured into water and the resulting precipitate was collected and dissolved in ethyl acetate. The organic solution was washed with water, dried over anhydrous magnesium sulfate, and filtered. The filtrate was evaporated under reduced pressure to leave a solid. The solid was purified by recrystallization from heptane to yield 0.52 g of 2-(2,4-dichlorophenyl)-4,6-dimethyl-1,2,4-triazine-3,5(2H,4H)-dione (mp 109-110°C), Compound 5 in the tables.

The nmr and ir spectra were consistent with the assigned structure.

EXAMPLE II2-[4-CHLORO-2-FLUORO-5-(1-METHYLETHOXY)PHENYL]-
1,2,4-TRIAZINE-3,5(2H,4H)-DIONE

5 Step A Methyl (2-chloro-4-fluorophenyl)
 carbonate

To a stirred solution of 20.0 g (0.14 mole) of 2-chloro-4-fluorophenol and 6.64 g (0.17 mole) of 10 sodium hydroxide in 100 mL of water at 15°C was added 17.7 g (0.19 mole) of methyl chloroformate. After complete addition, the mixture was stirred for 15 minutes then extracted with ethyl acetate. The organic phase was washed with a 1N sodium hydroxide solution, 15 then dried over anhydrous magnesium sulfate. The dried extract was filtered, and the filtrate evaporated under reduced pressure to provide methyl (2-chloro-4-fluorophenyl) carbonate as a solid.

20 Step B 2-Chloro-4-fluoro-5-nitrophenol

To a stirred mixture of methyl (2-chloro-4-fluorophenol) carbonate prepared in Step A in 21.7 mL of concentrated sulfuric acid was added dropwise 11.1 mL 25 of concentrated nitric acid. The reaction mixture was kept at a temperature below 30°C throughout the addition. After complete addition, the mixture was stirred at room temperature for one hour, then poured into 500 mL of ice water. The aqueous mixture was extracted 30 with ethyl acetate. The extract was washed in succession with water, saturated aqueous sodium bicarbonate, and saturated aqueous sodium chloride. The washed extract was dried over anhydrous magnesium sulfate, filtered, and the filtrate was evaporated under reduced 35 pressure to leave a solid residue, methyl (2-chloro-4-fluoro-5-nitrophenyl) carbonate. This residue was dissolved in 100 mL of ethanol to which was added 150

- 23 -

mL of a 1N sodium hydroxide solution. The mixture was heated on a steam bath for 30 minutes, cooled, and poured into a mixture of ice and hydrochloric acid. The resultant acidic mixture was extracted with ethyl acetate. The extract was dried over anhydrous magnesium sulfate and was filtered. The filtrate was evaporated under reduced pressure to give an oil which crystallized slowly. Recrystallization from heptane gave 15.8 g of 2-chloro-4-fluoro-5-nitrophenol.

10 The nmr spectrum was consistent with the assigned structure.

Step C 4-Chloro-2-fluoro-5-(1-methylethoxy)-nitrobenzene

15 To a stirred solution of 15.8 g (0.083 mole) of 2-chloro-4-fluoro-5-nitrophenol in 90 mL of acetone was added 17.1 g (0.12 mole) of potassium carbonate followed by a solution of 21.0 g (0.12 mole) of 2-iodopropane 20 in 10 mL of acetone. After complete addition, the reaction mixture was heated at 60°C for approximately 18 hours. The mixture was cooled and poured into a mixture of ice and concentrated hydrochloric acid. The resultant mixture was extracted with ethyl acetate, and 25 the extract was washed with a 1N sodium hydroxide solution. The washed extract was dried over anhydrous magnesium sulfate and was filtered. The solvent was evaporated under reduced pressure to leave 17.7 g of 4-chloro-2-fluoro-5-(1-methylethoxy)nitrobenzene as a 30 solid.

Step D 2-[4-Chloro-2-fluoro-5-(1-methylethoxy)-phenyl]-1,2,4-triazine-3,5(2H,4H)-dione

35 Hydrogenation of 2.8 g (0.012 mole) of 4-chloro-2-fluoro-5-(1-methylethoxy)nitrobenzene in the presence of 30 mL of acetic acid and 0.2 g of platinum oxide

produced 4-chloro-2-fluoro-5-(1-methylethoxy)aniline, which was not isolated from the reaction mixture. The platinum catalyst was removed by filtration, and the filtrate was diluted with 100 mL of water and 10 mL of concentrated hydrochloric acid. The acid solution was cooled to 0°C, and a solution of 0.84 g (0.012 mole) of sodium nitrite in 10 mL of water was added. The solution was stirred at 0°C for 30 minutes, then a solution of 5.0 g (0.061 mole) of sodium acetate in 10 mL of water was added. After stirring for a short period of time, the solution was added to a mixture of 3.0 g (0.12 mole) of malonyldiurethane [prepared by the method of Backes, et al., J. Chem. Soc., 359, (1921)] and 25.0 g (0.29 mole) of anhydrous sodium acetate in 300 mL of water at 10°C. After complete addition, the mixture was stirred at 10°C for 30 minutes. The mixture was extracted with ethyl acetate, and the extract washed with a saturated aqueous sodium chloride solution. The washed extract was dried over anhydrous magnesium sulfate, filtered, and the filtrate evaporated under reduced pressure to give 6.0 g of a solid.

The solid was dissolved in a mixture of 80 mL of ethanol and 80 mL of tetrahydrofuran. To this was added 40 mL of a 10% aqueous potassium hydroxide solution. The resultant mixture was stirred for 15 minutes and washed with ethyl acetate. The aqueous phase was made acidic with dilute hydrochloric acid, and the acidic solution extracted with ethyl acetate. The extract was treated with decolorizing charcoal and dried over anhydrous magnesium sulfate. The extract was filtered, and the filtrate was concentrated under reduced pressure to leave 3.2 g of a residue. The residue was heated at 150°C in 6.0 mL of mercaptoacetic acid for three hours. The mixture was cooled to room temperature, diluted with ethyl acetate, and extracted with a saturated aqueous sodium bicarbonate solution. The organic phase was dried over anhydrous magnesium

- 25 -

sulfate and filtered. The solvent was evaporated from the filtrate under reduced pressure to yield 2.0 g of 2-[4-chloro-2-fluoro-5-(1-methylethoxy)phenyl]-1,2,4-triazine-3,5(2H,4H)-dione as an oil, Compound 17 in the 5 tables.

The nmr spectrum was consistent with the assigned structure.

EXAMPLE III

10 2-[2,4-DICHLORO-5-(2-PROPYNYLOXY)PHENYL]-4-METHYL-1,2,4-TRIAZINE-3,5(2H,4H)-DIONE

Step A 3-Hydroxyacetanilide

- 15 To a stirred solution of 66.0 g (0.60 mole) of 3-amino-phenol in 180 mL of water was added dropwise 77.9 g (0.76 mole) of acetic anhydride. After complete addition, the reaction mixture was heated on a steam bath for 10 minutes, then cooled to 0°C. A precipitate
20 formed and was collected by filtration. The filter cake was washed with cold water and dried in a desiccator for two hours to yield 81.0 g of 3-hydroxyacetanilide (mp 144-146°C).

25 Step B 2,4-Dichloro-5-hydroxyacetanilide

- Chlorination of 53.0 g (0.35 mole) of 3-hydroxyacetanilide with chlorine gas in 400 mL of glacial acetic acid at 15-20°C for one hour produced 23.5 g of
30 2,4-dichloro-5-hydroxyacetanilide (mp 226-228°C).

Step C 2,4-Dichloro-5-(1-methylethoxy)acetanilide

- A stirred mixture of 22.0 g (0.1 mole) of 2,4-di-
35 chloro-5-hydroxyacetanilide, 25.5 g (0.15 mole) of 2-iodopropane, and 20.7 g (0.15 mole) of potassium

carbonate in 150 mL of acetone was heated at reflux temperature for approximately 18 hours. The mixture was cooled, filtered, and the filtrate evaporated under reduced pressure to leave a solid. The solid was 5 recrystallized from ethanol to yield 22.3 g of 2,4-di-chloro-5-(1-methylethoxy)acetanilide (mp 129-130°C).

Step D 2,4-Dichloro-5-(1-methylethoxy)aniline

10 A stirred mixture of 22.3 g of 2,4-dichloro-5-(1-methylethoxy) acetanilide, 60 mL of concentrated hydrochloric acid, and 60 mL of water was heated at reflux for 0.5 hour. The mixture was cooled in a refrigerator, and the resulting precipitate was collected by 15 filtration. The solid was suspended in water, and the mixture was treated with sodium carbonate until it was slightly basic. The resultant mixture was extracted with diethyl ether. The extract was washed with water, and the ether removed by distillation under reduced 20 pressure to leave an oil. Distillation of the oil under reduced pressure produced 14.0 g of 2,4-di-chloro-5-(1-methylethoxy)aniline (bp 102°C at 0.1 mm Hg).

25 Step E 2-[2,4-Dichloro-5-(1-methylethoxy)-phenyl]-1,2,4-triazine-3,5(2H,4H)-dione-6-carboxylic acid

To a stirred mixture of 10.0 g (0.045 mole) of 2,4-di-chloro-5-(1-methylethoxy)aniline in 200 mL of water was 30 added 30 mL of concentrated hydrochloric acid. The resultant mixture was cooled to 0°C, and a solution of 3.13 g (0.45 mole) of sodium nitrite in 30 mL of water was added during 15 minutes. After complete addition, 35 30.0 g (0.35 mole) sodium acetate in 60 mL of water was added, and the resulting mixture was stirred at 0°C for one hour. The cold reaction mixture was added por-

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tionwise to a stirred solution of 11.7 g (0.0477 mole) of malonyldiurethane [prepared by the method of Backes, et al., J. Chem. Soc., 350, (1921)] and 50.0 g (0.59 mole) of anhydrous sodium acetate in 1500 mL of water
5 at 0°C. After complete addition the mixture was stirred at 0°C for one hour, and the resulting precipitate was collected by filtration and washed with water. The filter cake was dissolved in a mixture of 250 mL of tetrahydrofuran and 250 mL of ethanol. To
10 this solution was added 150 mL of a 10% aqueous potassium hydroxide solution. The resultant mixture was stirred for 0.5 hour and made acidic with 60 mL of concentrated hydrochloric acid. Most of the tetrahydrofuran was removed from the mixture by evaporation under
15 reduced pressure to leave an aqueous residue. The residue was extracted with ethyl acetate, and the extract treated with decolorizing charcoal. The extract was dried over anhydrous magnesium sulfate and filtered. The filtrate was evaporated under reduced
20 pressure to leave 17.9 g of 1-[2,4-dichloro-5-(1-methylethoxy)phenyl]-1,2,4-triazine-3,5(2H,4H)-dione-6-carboxylic acid, Compound 11 in the tables.

The preparation of Compound 11 was repeated. The product was found to have a melting point of 195-197°C
25 (dec.) and its nmr and ir spectra were consistent with the assigned structure.

Step F 2-[2,4-Dichloro-5-(1-methylethoxy)phenyl]-
 1,2,4-triazine-3,5(2H,4H)-dione
30

A stirred mixture of 10.0 g (0.028 mole) of 2-[2,4-dichloro-5-(1-methylethoxy)phenyl]-1,2,4-triazine-3,5(2H,4H)-dione-6-carboxylic acid in 10 mL of mercaptoacetic acid was heated at 140°C for two hours. The
35 reaction mixture was cooled to room temperature and partitioned between ethyl acetate and saturated aqueous sodium bicarbonate. The organic phase was washed with

two portions of saturated aqueous sodium bicarbonate, and then with saturated aqueous sodium chloride. The washed organic phase was dried over anhydrous magnesium sulfate and filtered. The filtrate was evaporated 5 under reduced pressure to yield 7.5 g of 2-[2,4-dichloro-5-(1-methylethoxy)phenyl]-1,2,4-triazine-3,5(2H,4H)-dione, Compound 51 in the tables.

Compound 6 in the tables was prepared in a similar manner (Step E and F) from the appropriately substituted aniline. 10

Step G 2-[2,4-Dichloro-5-(1-methylethoxy)phenyl]-4-methyl-1,2,4-triazine-3,5(2H,4H)-dione

15 To a stirred mixture of 0.6 g (0.025 mole) of sodium hydride in 15 mL of N,N-dimethylformamide was added a solution of 7.5 g (0.024 mole) of 2-[2,4-dichloro-5-(1-methylethoxy)phenyl]-1,2,4-triazine-3,5(2H,4H)-dione in 30 mL of N,N-dimethylformamide with external cooling 20 to maintain the reaction temperature below 40°C. After complete addition, the mixture was allowed to come to room temperature and was stirred for one hour. A solution of 3.5 g (0.025 mole) of iodomethane in 10 mL of N,N-dimethylformamide was added to the reaction mixture, and stirring was continued for an additional hour 25 at room temperature. The reaction mixture was poured into ice water, and the mixture was extracted with ethyl acetate. The extract was dried over anhydrous magnesium sulfate and filtered. The filtrate was evaporated under reduced pressure to produce 2-[2,4-di- 30 chloro-5-(1-methylethoxy)phenyl]-4-methyl-1,2,4-triazine-3,5(2H,4H)-dione as an oil, Compound 12 in the tables.

The preparation of Compound 12 was repeated. The product was found to have a melting point of 111-112°C 35 after chromatographic purification on a silica gel column. The nmr and ir spectra of this sample were

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consistent with the assigned structure. Compounds 2, 7, 8, and 18 were also prepared in this manner from the appropriately substituted anilines (prepared by the methods of Example III, Steps E and F) and iodo-
5 methane. Compounds 3, 15 and 19 were prepared from 3-bromo-1-propene and the appropriately substituted triazinedione. Similarly, reaction of the appropriately substituted triazinedione with propargyl bromide, bromoethane, and 1-chloro-2-fluoroethane gave Compounds
10 25, 29, and 41 respectively.

Step H 2-(2,4-Dichloro-5-hydroxyphenyl)-4-methyl-
 1,2,4-triazine-3,5(2H,4H)-dione

15 The oil prepared in Step G (Compound 12) was stirred with 10 mL of concentrated sulfuric acid at 0°C for 10 minutes, and the mixture was poured into ice water. The aqueous mixture was extracted with ethyl acetate, and the solvent was removed from the extract by evaporation under reduced pressure to give a residue. The residue was purified by column chromatography on silica gel, eluting with ethyl acetate:heptane (1:1). Evaporation of the appropriate fractions gave 4.4 g of
20 2-(2,4-dichloro-5-hydroxyphenyl)-4-methyl-1,2,4-triazine-3,5(2H,4H)-dione (mp 199-201°C), Compound 9 in
25 the tables.

The nmr spectrum was consistent with the assigned structure.

30 Step I 2-[2,4-Dichloro-5-(2-propynyoxy)phenyl]-
 4-methyl-1,2,4-triazine-3,5(2H,4H)-dione

Under a dry nitrogen atmosphere a solution of 1.0 g (0.003 mole) of 2-(2,4-dichloro-5-hydroxyphenyl)-4-
35 methyl-1,2,4-triazine-3,5(2H,4H)-dione in 15 mL of N,N-dimethylformamide was added slowly to a stirred mixture of 0.09 g (0.0037 mole) of sodium hydride in 15

- 30 -

mL of N,N-dimethylformamide. After complete addition, the mixture was stirred at 28°C until hydrogen evolution ceased, then at 45°C for 30 minutes. The reaction mixture was cooled to room temperature, and a solution 5 of 0.57 g (0.0038 mole) of 3-bromo-1-propyne in 5 mL of N,N-dimethylformamide was added. The mixture was stirred at room temperature for approximately 18 hours, poured into water, and extracted with ethyl acetate. The extract was washed with a saturated aqueous sodium 10 chloride solution, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed from the filtrate by evaporation under reduced pressure to leave an oil. The oil was purified by preparative chromatography on silica gel, eluting with ethyl acetate:heptane (1:1), to yield 0.8 g of 2-[2,4-di- 15 chloro-5-(2-propynyoxy)phenyl]-4-methyl-1,2,4-triazine-3,5(2H,4H)-dione (mp 119-120°C), Compound 20 in the tables.

The nmr and ir spectra were consistent with the 20 assigned structure.

Compound 21, 2-[4-chloro-2-fluoro-5-(2-propynyl-oxy)phenyl]-4-methyl-1,2,4-triazine-3,5(2H,4H)-dione, was also prepared by the method of Example III, Steps H and I, from the appropriately substituted triazinedione. 25

EXAMPLE IV

2-[2,4-DICHLORO-5-(1-METHYLETHOXY)PHENYL]- 4,6-DIMETHYL-1,2,4-TRIAZINE-3,5(2H,4H)-DIONE

30 Step A 2,4-Dichloro-5-(1-methylethoxy)phenyl-hydrazine

A solution of 15.8 g (0.23 mole) of sodium nitrite in 100 mL of water was added to a stirred solution of 50.0 35 g (0.23 mole) of 2,4-dichloro-5-(1-methylethoxy)aniline in 250 mL of concentrated hydrochloric acid at 0°C over 30 minutes. After complete addition, the mixture was

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stirred at 0°C for 30 minutes. A solution of 114.0 g (0.506 mole) of tin (II) chloride dihydrate in 125 mL of concentrated hydrochloric acid was added dropwise to the reaction mixture. After complete addition, the
5 mixture was stirred for one hour. The resultant white slurry was filtered. The filter cake was added to a 20% aqueous sodium hydroxide solution and stirred for 30 minutes. The basic mixture was filtered, and the filter cake recrystallized from methanol and water to
10 yield 37.0 g of 2,4-dichloro-5-(1-methylethoxy)phenyl-hydrazine.

Step B 1-[2,4-Dichloro-5-(1-methylethoxy)phenyl]-
 3,3-dimethyl-1,2,4-triazolidin-5-one

15

To a stirred solution of 12.7 g (0.054 mole) of 2,4-di-chloro-5-(1-methylethoxy)phenylhydrazine in a mixture of 100 mL of tetrahydrofuran and 30 mL of acetone was added 0.5 mL of a 2N sulfuric acid solution. The reac-
20 tion mixture was stirred at room temperature for 30 minutes after which the solvent was removed by evapo-
tation under reduced pressure. The residue was dissolved in ethyl acetate, and the organic solution was washed with water. The washed organic solution was dried over
25 anhydrous magnesium sulfate, filtered, and the filtrate evaporated under reduced pressure leaving 14.6 g of an oil. The oil was dissolved in 50 mL of glacial acetic acid and 2 mL of water. To this solution was added portionwise 4.5 g (0.56 mole) of potassium cyanate.
30 After complete addition, the mixture was stirred at room temperature for approximately 18 hours. An addi-
tional 0.5 g of potassium cyanate was added, and the reaction mixture was stirred for five hours. The mix-
ture was then diluted with water and extracted with
35 ethyl acetate. The extract was dried over anhydrous magnesium sulfate, filtered, and the filtrate evapo-
rated under reduced pressure leaving an oil. The oil

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was dissolved in 20 mL of ethyl acetate and, upon the addition of 10 mL of heptane, formed a precipitate. The precipitate was collected by filtration and recrystallized from ethyl acetate and heptane to give 5 4.5 g of 1-[2,4-dichloro-5-(1-methylethoxy)phenyl]-3,3-dimethyl-1,2,4-triazolidin-5-one (mp 162-163°C).

The nmr and ir spectra were consistent with the assigned structure.

10 Step C 2-[2,4-Dichloro-5-(1-methylethoxy)phenyl]-6-methyl-1,2,4-triazine-3,5(2H,4H)-dione

To a stirred mixture of 1.0 g (0.0031 mole) of 1-[2,4-dichloro-5-(1-methylethoxy)phenyl]-3,3-dimethyl-1,2,4-15 triazolidin-5-one in 10 mL of p-dioxane was added 0.29 g (0.0031 mole) of pyruvic acid and one drop of concentrated sulfuric acid. The mixture was stirred at room temperature for one hour, then an additional 0.25 g (0.0029 mole) of pyruvic acid was added. The mixture 20 was heated at 90°C for three hours, then poured into water. The mixture was extracted with ethyl acetate, and the solvent was evaporated from the extract under reduced pressure to give an oil. The oil was purified by thin-layer preparative chromatography on silica gel, 25 eluting with ethyl acetate:heptane (1:1). Extraction of the appropriate bands gave 0.6 g of 2-[2,4-dichloro-5-(1-methylethoxy)phenyl]-6-methyl-1,2,4-triazine-3,5(2H,4H)-dione as a solid (mp 163-164°C), Compound 10 in the tables.

30 The nmr and ir spectra were consistent with the assigned structure.

Step D 2-[2,4-Dichloro-5-(1-methylethoxy)phenyl]-4,6-dimethyl-1,2,4-triazine-3,5(2H,4H)-35 dione

In a manner similar to Example III, Step G, the reac-

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tion of 0.28 g (0.00085 mole) of 2-[2,4-dichloro-5-(1-methylethoxy)phenyl]-6-methyl-1,2,4-triazine-3,5(2H,4H)-dione with 0.037 g (0.00093 mole) of sodium hydride (60% in oil) and 0.13 g (0.00093 mole) of iodomethane 5 in 10 mL of N,N-dimethylformamide produced 0.19 g of 2-[2,4-dichloro-5-(1-methylethoxy)phenyl]-4,6-dimethyl-1,2,4-triazine-3,5(2H,4H)-dione as a low melting solid, Compound 13 in the tables.

The nmr and ir spectra were consistent with the 10 assigned structure.

Compound 16, 2-[2,4-dichloro-5-(1-methylethoxy)-phenyl]-6-methyl-4-(2-propenyl)-1,2,4-triazine-3,5-(2H,4H)-dione, was also prepared by the method of Example IV using 3-bromo-1-propene rather than iodo-15 methane in Step D. Similarly, Compound 50, 2-[4-chloro-2-fluoro-5-(1-methylethoxy)phenyl]-4-(3-fluoropropyl)-1,2,4-triazine-3,5(2H,4H)-dione, was prepared by treating Compound 17 (Example II D) with 1-chloro-3-fluoropropane.

20

EXAMPLE V

2-[2,4-DICHLORO-5-(1-METHYLETHOXY)PHENYL]-4-METHYL-1,2,4-TRIAZINE-3,5(2H,4H)-DIONE-6-CARBOXYLIC ACID

25 In a manner similar to Example III, Step G, the reaction of 6.6 g (0.018 mole) of 2-[2,4-dichloro-5-(1-methylethoxy)phenyl]-1,2,4-triazine-3,5(2H,4H)-dione-6-carboxylic acid (Compound 11, Example III E) with 1.5 g (0.037 mole) of sodium hydride (60% in oil) and 2.6 g 30 (0.018 mole) of iodomethane in 35 mL of N,N-dimethyl-formamide produced 2.1 g of 2-[2,4-dichloro-5-(1-methylethoxy)phenyl]-4-methyl-1,2,4-triazine-3,5-(2H,4H)-dione-6-carboxylic acid as a solid (mp 230°C d), Compound 14 in the tables.

35 The nmr and ir spectra were consistent with the assigned structure.

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EXAMPLE VI

ETHYL 2,4-DICHLORO-5-[4-METHYL-1,2,4-TRIAZINE-3,5(2H,4H)-DIONE-2-YL]PHENOXYACETATE

5 In a manner similar to Example II, Step C, the reaction of 0.86 g (0.0030 mole) of 2-(2,4-dichloro-5-hydroxyphenyl)-4-methyl-1,2,4-triazine-3,5(2H,4H)-dione (Compound 9, Example III H) with 0.62 g (0.0045 mole) of potassium carbonate and 0.75 g (0.0045 mole) of ethyl bromoacetate in 10 mL of acetone produced an oil. The oil crystallized upon treatment with heptane to yield 0.85 g of ethyl 2,4-dichloro-5-[4-methyl-1,2,4-triazine-3,5(2H,4H)-dione-2-yl]phenoxyacetate (mp 115-117°C), Compound 22 in the tables.

15 The nmr and ir spectra were consistent with the assigned structure.

Compounds 27 and 28 were prepared in a similar manner by treatment of Compound 9 with ethyl 2-bromo-propionate and chloroacetonitrile respectively. The 20 nmr and ir spectra were consistent with the assigned structures.

EXAMPLE VII

2-(2,4-DICHLORO-5-METHYLSULFONYLOXYPHENYL)-4-METHYL-1,2,4-TRIAZINE-3,5(2H,4H)-DIONE

A solution of 0.35 g (0.0031 mole) of methanesulfonyl chloride in 5 mL of tetrahydrofuran was added to a stirred solution of 0.8 g (0.0028 mole) of 2-(2,4-dichloro-5-hydroxyphenyl)-4-methyl-1,2,4-triazine-3,5(2H,4H)-dione (Compound 9, Example III H) and 0.30 g (0.0031 mole) of triethylamine in 10 mL of tetrahydrofuran. The reaction mixture was stirred at room temperature for approximately 18 hours, then diluted 35 with water. The resultant mixture was extracted with ethyl acetate, and the extract was dried over anhydrous magnesium sulfate. The dried extract was filtered, and

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the filtrate was evaporated under reduced pressure to give 0.81 g. of 2-(2,4-dichloro-5-methylsulfonyloxyphenyl)-4-methyl-1,2,4-triazine-3,5(2H,4H)-dione as a solid, Compound 23 in the tables.

5 The nmr and ir spectra were consistent with the assigned structure.

EXAMPLE VIII

10 2-[2,4-DICHLORO-5-(1-METHYLETHOXY)PHENYL]-4-(2-FLUOROETHYL)-1,2,4-TRIAZINE-3,5(2H,4H)-DIONE

To a stirred mixture of 0.084 g (0.0035 mole) of sodium hydride in 20 mL of tetrahydrofuran was added a solution of 1.0 g (0.003 mole) of 2-[2,4-dichloro-5-(1-methylethoxy)phenyl]-1,2,4-triazine-3,5(2H,4H)-dione (Compound 51, Example III, Step F) in 5 mL of tetrahydrofuran. The resulting mixture was stirred at room temperature for one hour. Tetrabutylammonium bromide (0.5 g, 0.002 mole) and potassium hydroxide (0.5 g, 0.009 mole) were added, and the mixture was heated at 60-70°C for approximately 1.5 hours. While maintaining the temperature at 60°C, a solution of 0.5 g (0.004 mole) of 1-bromo-2-fluoroethane in 5 mL of tetrahydrofuran was added. After complete addition, the mixture was allowed to cool to room temperature and was stirred for approximately 18 hours. The mixture was partitioned between dilute aqueous hydrochloric acid and ethyl acetate. The organic phase was dried over anhydrous magnesium sulfate and filtered. Evaporation of the filtrate under reduced pressure produced an oil. The oil was subjected to column chromatography on silica gel, eluting with ethyl acetate:n-heptane (1:1). Evaporation of the appropriate fractions provided a solid which was recrystallized from ethyl acetate:n-heptane to give 0.4 g of 2-[2,4-dichloro-5-(1-methylethoxy)phenyl]-4-(2-fluoroethyl)-1,2,4-triazine-3,5(2H,4H)-dione, Compound 26 in the tables.

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The nmr spectrum was consistent with the assigned structure.

EXAMPLE IX

5 2-[4-CHLORO-2-FLUORO-5-(3-BROMO-2-PROPYNYLOXY)-
PHENYL]-4-METHYL-1,2,4-TRIAZINE-3,5(2H,4H)-DIONE

To a stirred mixture of 0.05 g (0.002 mole) of sodium hydride in 5 mL of tetrahydrofuran was added a solution 10 of 0.55 g (0.0018 mole) of 2-[4-chloro-2-fluoro-5-(2-propynyloxy)phenyl]-4-methyl-1,2,4-triazine-3,5(2H,4H)-dione (Compound 21, see Example III, Step J) in 5 mL of tetrahydrofuran. To this mixture was added a solution of 0.28 g (0.0018 mole) of bromine in 5 mL 15 of tetrahydrofuran. After complete addition, the reaction mixture was stirred at room temperature for one hour. Water, 5 mL, was added to the mixture, and the total stirred at room temperature for two days. The mixture was partitioned between water and ethyl 20 acetate. The organic phase was dried over anhydrous magnesium sulfate and filtered. The filtrate was evaporated under reduced pressure to yield 0.45 g of 2-[4-chloro-2-fluoro-5-(3-bromo-2-propynyloxy)phenyl]-4-methyl-1,2,4-triazine-3,5(2H,4H)-dione as a solid (mp 25 127-129°C), Compound 48 in the tables.

The nmr spectrum was consistent with the assigned structure.

EXAMPLE X

30 METHYL 2-[2-CHLORO-4-FLUORO-5-(2,3,4,5-TETRAHYDRO-
4-METHYL-3,5-DIOXO-1,2,4-TRIAZIN-2-YL)PHENOXY]-
PROPIONATE

Step A 2-(4-Chloro-2-fluoro-5-hydroxyphenyl)-
35 4-methyl-1,2,4-triazine-3,5(2H,4H)-dione

Treatment of 2-[4-chloro-2-fluoro-5-(1-methylethoxy)-

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phenyl]-4-methyl-1,2,4-triazine-3,5(2H,4H)-dione
(Compound 18, see Example III G) with sulfuric acid in
the manner of Example III H produced the phenolic
compound 2-(4-chloro-2-fluoro-5-hydroxyphenyl)-4-
5 methyl-1,2,4-triazine-3,5(2H,4H)-dione, Compound 30 in
the tables.

The nmr spectrum was consistent with the assigned
structure.

10 Step B Methyl 2-[2-chloro-4-fluoro-5-(2,3,4,5-
tetrahydro-4-methyl-3,5-dioxo-1,2,4-
triazin-2-yl)phenoxy]propionate

Treatment of Compound 30 with methyl 2-chloropropionate
15 in the presence of potassium carbonate in the manner of
Example VI gave methyl 2-[2-chloro-4-fluoro-5-(2,3,4,5-
tetrahydro-4-methyl-3,5-dioxo-1,2,4-triazin-2-yl)phen-
oxy]propionate, Compound 42 in the tables.

The nmr spectrum was consistent with the assigned
20 structure.

Compounds 43, 44 and 49 were prepared in a similar
manner by treatment of 2-(4-chloro-2-fluoro-5-hydroxy-
phenyl)-4-methyl-1,2,4-triazine-3,5(2H,4H)-dione with
ethyl chloroacetate, propargyl bromide, and iodoacet-
25 amide respectively.

The nmr and ir spectra were consistent with the
assigned structures.

Other compounds of the invention may be prepared by
the methods exemplified above or by methods within the
30 skill of the art.

HERBICIDAL ACTIVITY

The plant test species used in demonstrating the
herbicidal activity of compounds of this invention
include cotton (Gossypium hirsutum var. Stoneville),
35 soybean (Glycine max var. Williams), field corn (Zea
mays var. Agway 595S), wheat (Triticum aestivum var.
Prodax), field bindweed (Convolvulus arvensis), morn-

ingglory (Ipomea lacunosa or Ipomea hederacea), velvet-leaf (Abutilon theophrasti), barnyardgrass (Echinochloa crus galli), green foxtail (Setaria viridis), and johnsongrass (Sorghum halepense).

5 Seeds or tubers of the plant test species were planted in furrows in steam sterilized sandy loam soil contained in disposable fiber flats. A topping soil of equal portions of sand and sandy loam soil was placed uniformly on top of each flat to a depth of approxi-
10 mately 0.5 cm.

The flats for the preemergence test were watered, then drenched with the appropriate amount of a solution of the test compound in a mixture of acetone and water containing a small amount (up to 0.5% v/v) of sorbitan monolaurate emulsifier/solubilizer. The concentration of the test compound in solution was varied to give a range of application rates, generally 8.0 kg/ha and submultiples thereof. The flats were placed in a greenhouse and watered regularly at the soil surface
15 for 21 days at which time phytotoxicity data were recorded.
20

The flats for the postemergence test were placed in a greenhouse and watered for 8-10 days, then the foliage of the emerged test plants was sprayed with a
25 solution of the test compound in acetone-water containing up to 0.5% sorbitan monolaurate. After spraying the foliage was kept dry for 24 hours, then watered regularly for 21 days, and phytotoxicity data recorded.

Phytotoxicity data were taken either as percent
30 kill or percent control. Percent control was determined by a method similar to the 0 to 100 rating system disclosed in "Research Methods In Weed Science," 2nd ed., B. Truelove, Ed.; Southern Weed Science Society; Auburn University, Auburn, Alabama, 1977. The present
35 rating system is as follows:

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Herbicide Rating System

<u>Rating Percent Control</u>	<u>Description of Main Categories</u>	<u>Crop Description</u>	<u>Weed Description</u>
0	No effect	No crop reduction or injury	No weed control
10		Slight discoloration or stunting	Very poor weed control
20	Slight effect	Some discoloration, stunting or stand loss	Poor weed control
30		Crop injury more pronounced but not lasting	Poor to deficient weed control
40		Moderate injury, crop usually recovers	Deficient weed control
50	Moderate effect	Crop injury more lasting, recovery	Deficient to moderate weed control
60		Lasting crop injury no recovery	Moderate weed control
70		Heavy injury and stand loss	Control somewhat less than satisfactory
80	Severe effect	Crop nearly destroyed a few survivors	Satisfactory to good weed control
90		Only occasional live plants left	Very good to excellent control
100	Complete effect	Complete crop destruction	Complete weed destruction

Herbicidal data at selected application rates are given for various compounds of the invention in Table 3 and Table 4 below. The test compounds are identified therein by numbers which correspond to those in Table 1.

5 In Tables 3 and 4 below:

"kg/ha" is kilograms per hectare,

"% K" is percent kill, and

"% C" is percent control.

It is clear from the data that the generic class of
10 aryltriazinediones and sulfur analogs thereof described
and illustrated herein is characterized by herbicidal
activity, and that the degree of this activity varies
among specific compounds within this class and to some
extent among the species of plant to which these com-
15 pounds may be applied. Thus, selection of a specific
herbicidal compound for control of a specific plant may
readily be made.

For herbicidal application, the active compounds as
above defined are formulated into herbicidal composi-
20 tions, by admixture, in herbicidally effective amounts,
with adjuvants and carriers normally employed in the
art for facilitating the dispersion of active ingre-
dients for the particular utility desired, recognizing
the fact that the formulation and mode of application
25 of a toxicant may affect the activity of the material
in a given application. Thus, for agricultural use the
present herbicidal compounds may be formulated as
granules of relatively large particle size, as water-
soluble or water-dispersible granules, as powdery
30 dusts, as wettable powders, as emulsifiable concen-
trates, as solutions, or as any of several other known
types of formulations, depending on the desired mode of
application.

For preemergence application these herbicidal
35 compositions are usually applied either as sprays,
dusts, or granules in the areas in which suppression of

vegetation is desired. For postemergence control of established plant growth, sprays or dusts are most commonly used. These formulations may contain as little as 0.5% to as much as 95% or more by weight of 5 active ingredient.

Dusts are free flowing admixtures of the active ingredient with finely divided solids such as talc, natural clays, kieselguhr, flours such as walnut shell and cottonseed flours, and other organic and inorganic 10 solids which act as dispersants and carriers for the toxicant; these finely divided solids have an average particle size of less than about 50 microns. A typical dust formulation useful herein is one containing 1.0 part of the herbicidal compound and 99.0 parts of talc.

15 Wettable powders, also useful formulations for both pre- and postemergence herbicides, are in the form of finely divided particles which disperse readily in water or other dispersant. The wettable powder is ultimately applied to the soil either as a dry dust or 20 as an emulsion in water or other liquid. Typical carriers for wettable powders include Fuller's earth, kaolin clays, silicas, and other highly absorbent, readily wet inorganic diluents. Wettable powders normally are prepared to contain about 5-80% of active 25 ingredient, depending on the absorbency of the carrier, and usually also contain a small amount of a wetting, dispersing or emulsifying agent to facilitate dispersion. For example, a useful wettable powder formulation contains 80.8 parts of the herbicidal compound, 30 17.9 parts of Palmetto clay, and 1.0 part of sodium lignosulfonate and 0.3 part of sulfonated aliphatic polyester as wetting agents. Frequently, additional wetting agent and/or oil will be added to the tank-mix for postemergence application to facilitate dispersion 35 on the foliage and absorption by the plant.

Other useful formulations for herbicidal applications are emulsifiable concentrates. Emulsifiable

- concentrates are homogeneous liquid or paste compositions dispersible in water or other dispersant, and may consist entirely of the herbicidal compound and a liquid or solid emulsifying agent, or may also contain
- 5 a liquid carrier, such as xylene, heavy aromatic naphthas, isophorone, or other non-volatile organic solvent. For herbicidal application these concentrates are dispersed in water or other liquid carrier, and normally applied as a spray to the area to be treated.
- 10 The percentage by weight of the essential active ingredient may vary according to the manner in which the composition is to be applied, but in general comprises 0.5 to 95% of active ingredient by weight of the herbicidal composition.
- 15 Typical wetting, dispersing, or emulsifying agents used in agricultural formulations include, for example, the alkyl and alkylaryl sulfonates and sulfates and their sodium salts, polyhydric alcohols, and other types of surface active agents, many of which are
- 20 available in commerce. The surface active agent, when used, normally comprises 1% to 15% by weight of the herbicidal composition.

Other useful formulations for herbicidal applications include simple solutions of the active ingredient

25 in a solvent in which it is completely soluble at the desired concentration, such as acetone, alkylated naphthalenes, xylene, or other organic solvents.

Granular formulations, wherein the toxicant is carried on relatively coarse particles, are of particular

30 utility for aerial distribution or for penetration of cover crop canopy. Pressurized sprays, typically aerosols wherein the active ingredient is dispersed in finely divided form as a result of vaporization of a low boiling dispersant solvent carrier, such as the

35 Freons, may also be used. Water-soluble or water-dispersible granules are also useful formulations for herbicidal application of the present compounds. Such

granular formulations are free-flowing, non-dusty, and readily water-soluble or water-miscible. The soluble or dispersible granular formulations described in U.S. patent No. 3,920,442 are useful herein with the present 5 herbicidal compounds.

The active herbicidal compounds of this invention may be formulated and/or applied with insecticides, fungicides, nematicides, plant growth regulators, fertilizers, or other agricultural chemicals and may be 10 used as effective soil sterilants as well as selective herbicides in agriculture. In applying an active compound of this invention, whether formulated alone or with other agricultural chemicals, an effective amount and concentration of the active compound is of course 15 employed.

The active herbicidal compounds of this invention may be used in combination with other herbicides, e.g. they may be mixed with, say, an equal or larger amount of a known herbicide such as chloroacetanilide herbicides such as 2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide (alachlor), 2-chloro-N(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide (metolachlor), and N-chloroacetyl-N-(2,6-diethyl-phenyl)glycine (diethyl-ethyl); benzothiadiazinone 25 herbicides such as 3-(1-methylethyl)-(1H)-2,1,3-benzothiadiazin-4-(3H)-one-2,2-dioxide (bentazon); triazine herbicides such as 6-chloro-N-ethyl-N-(1-methylethyl)-1,3,5-triazine-2,4-diamine (atrazine), and 2-[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino-2- 30 methylpropanenitrile (cyanazine); dinitroaniline herbicides such as 2,6-dinitro-N,N-dipropyl-4-(trifluoromethyl)benzeneamine (trifluralin); and aryl urea herbicides such as N'-(3,4-dichlorophenyl)-N,N-dimethylurea (diuron) and N,N-dimethyl-N'-(3-(trifluoro- 35 methyl)phenyl)urea (fluometuron).

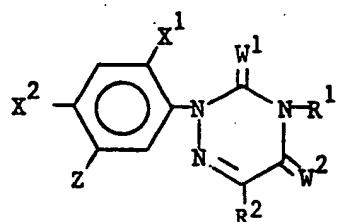
It is apparent that various modifications may be made in the formulation and application of the com-

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pounds of this invention without departing from the inventive concepts herein as defined in the claims.

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Table 1
Representative Compounds



(Except where indicated otherwise, W¹ = W² = oxygen).

Compound Number	X¹	X²	Z	R¹	R²
1	H	H	H	CH ₃	H
2	F	H	H	CH ₃	H
3	H	C1	H	CH ₂ CH=CH ₂	H
4	C1	C1	H	H	CH ₃
5	C1	C1	H	CH ₃	CH ₃
6	F	C1	H	H	H
7	F	C1	H	CH ₃	H
8⁴	C1	C1	H	CH ₃	H
9	C1	C1	OH	CH ₃	H
10	C1	C1	OCH(CH ₃) ₂	H	CH ₃
11	C1	C1	OCH(CH ₃) ₂	H	CO ₂ H
12	C1	C1	OCH(CH ₃) ₂	CH ₃	H
13	C1	C1	OCH(CH ₃) ₂	CH ₃	CH ₃
14	C1	C1	OCH(CH ₃) ₂	CH ₃	CO ₂ H
15	C1	C1	OCH(CH ₃) ₂	CH ₂ CH=CH ₂	H
16	C1	C1	OCH(CH ₃) ₂	CH ₂ CH=CH ₂	CH ₃
17	F	C1	OCH(CH ₃) ₂	H	H
18	F	C1	OCH(CH ₃) ₂	CH ₃	H
19	F	C1	OCH(CH ₃) ₂	CH ₂ CH=CH ₂	H
20	C1	C1	OCH ₂ C≡CH	CH ₃	H
21	F	C1	OCH ₂ C≡CH	CH ₃	H
22	C1	C1	OCH ₂ CO ₂ C ₂ H ₅	CH ₃	H
23	C1	C1	OSO ₂ CH ₃	CH ₃	H
24 ¹	F	C1	OCH ₂ C≡CH	CH ₃	H

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Table 1
Representative Compounds

<u>Compound Number</u>	<u>X¹</u>	<u>X²</u>	<u>Z</u>	<u>R¹</u>	<u>R²</u>
25	Cl	Cl	OCH(CH ₃) ₂	CH ₂ C≡CH	H
26	Cl	Cl	OCH(CH ₃) ₂	CH ₂ CH ₂ F	H
27	Cl	Cl	OCH(CH ₃)CO ₂ C ₂ H ₅	CH ₃	H
28	Cl	Cl	OCH ₂ CN	CH ₃	H
29	Cl	Cl	OCH(CH ₃) ₂	C ₂ H ₅	H
30	F	Cl	OH	CH ₃	H
31	H	Cl	H	H	CO ₂ H
32	H	Cl	OCH ₃	H	CO ₂ H
33	H	Cl	H	H	H
34	H	CH ₃	H	H	H
35	H	CH ₃	H	CH ₃	H
36	H	Cl	H	CH ₃	H
37	H	Cl	OCH ₃	H	H
38	H	OCH ₃	H	H	H
39	H	Cl	OCH ₃	CH ₃	H
40	H	OCH ₃	H	CH ₃	H
41	F	Cl	OCH(CH ₃) ₂	CH ₂ F	H
42	F	Cl	OCH(CH ₃)CO ₂ CH ₃	CH ₃	H
43	F	Cl	OCH ₂ CO ₂ C ₂ H ₅	CH ₃	H
44	F	Cl	OCH ₂ C≡CH	CH ₂ F	H
45	F	Cl	OCH(CH ₃) ₂	CH ₂ CN	H
46	F	Cl	NO ₂	CH ₃	H
47	F	Cl	NH ₂	CH ₃	H
48	F	Cl	OCH ₂ C≡CBr	CH ₃	H
49	F	Cl	OCH ₂ CONH ₂	CH ₃	H
50	F	Cl	OCH(CH ₃) ₂	CH ₂ (CH ₂) ₂ F	H
51	Cl	Cl	OCH(CH ₃) ₂	H	H
52	F	Cl	OCH ₂ C≡CI	CH ₃	H
53	F	Br	OCH(CH ₃) ₂	CH ₃	H
54	F	H	OCH(CH ₃) ₂	CH ₃	H
55	F	CH ₃	OCH(CH ₃) ₂	CH ₃	H

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Table 1
Representative Compounds

Compound Number	X ¹	X ²	Z	R ¹	R ²
56	F	CF ₃	OCH ₂ C≡CH	CH ₃	H
57	F	OC ₆ H ₅	OCH ₂ C≡CH	CH ₃	H
58	F	OCH ₂ C ₆ H ₅	OCH(CH ₃) ₂	CH ₃	H
59	F	C1	NHCH ₃	CH ₃	H
60	F	C1	N(CH ₃) ₂	CH ₃	H
61 ¹	F	C1	OSO ₂ CH ₃	CH ₃	H
62	F	C1	CO ₂ H	CH ₃	H
63	F	C1	CO ₂ CH ₃	CH ₃	H
64	F	C1	CO ₂ C ₂ H ₅	CH ₃	H
65	F	C1	CO-SCH ₃	CH ₃	H
66	F	C1	CO ₂ CH ₂ CH ₂ OCH ₃	CH ₃	H
67	F	C1	CONH ₂	CH ₃	H
68	F	C1	CONHCH ₃	CH ₃	H
69	F	C1	CON(CH ₃) ₂	CH ₃	H
70	F	C1	CONHCH ₂ CH ₂ OCH ₃	CH ₃	H
71	F	C1	CON(CH ₃)CH ₂ CH ₂ OCH ₃	CH ₃	H
72	F	C1	OCH(CH ₃) ₂	CH ₂ C≡CH	H
73	F	C1	OCH(CH ₃) ₂	NH ₂	H
74	F	C1	OCH ₂ C≡CH	CH ₂ CN	H
75	F	C1	NHCHCONHCHCH ₃ CH ₃ C ₂ H ₅	CH ₃	H
76	F	C1	OCHCONHCHCH ₃ CH ₃ C ₂ H ₅	CH ₃	H
77	F	C1	CH ₃	CH ₃	H
78	F	C1	O- 	CH ₃	H
79	F	C1	CF ₃	CH ₃	H
80	F	C1	SH	CH ₃	H
81	F	C1	SO ₃ H	CH ₃	H
82	F	C1	SCH ₃	CH ₃	H

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Table 1
Representative Compounds

Compound Number	X ¹	X ²	Z	R ¹	R ²
83	F	C1	SOCH ₃	CH ₃	H
84	F	C1	SO ₂ CH ₃	CH ₃	H
85	F	C1	SCH(CH ₃) ₂	CH ₃	H
86	F	C1	SCH ₂ C=CH	CH ₃	H
87	F	Br	NHCH(CH ₃)CO ₂ C ₂ H ₅	CH ₃	H
88	F	C1	NHCH(CH ₃)CONHCH ₃	CH ₃	H
89	F	C1	NHCH(CH ₃) ₂	CH ₃	H
90	F	C1	NHCH ₂ C=CH	CH ₃	H
91	F	C1	NH— 	CH ₃	H
92	F	C1	NHCOCH ₃	CH ₃	H
93	F	C1	NHCO ₂ CH ₃	CH ₃	H
94	F	C1	O— 	CH ₃	H
95	F	C1	OCF ₂ H	CH ₃	H
96	F	C1	OCH ₂ OCH ₃	CH ₃	H
97	F	C1	O— 	CH ₃	H
98	F	C1	OCH ₂ — 	CH ₃	H
99	F	C1	OCH ₂ — 	CH ₃	H
100	F	C1	OCH ₂ — 	CH ₃	H
101	F	C1	O— 	CH ₃	H
102	F	C1	O— 	CH ₃	H
103	F	C1	O— 	CH ₃	H

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Table 1
Representative Compounds

Compound Number	X ¹	X ²	Z	R ¹	R ²
104	F	C1	O-C(=O)c1ccccc1S(=O)(=O)C	CH ₃	H
105	F	C1	O-C(=O)c1cc(N-CH ₃)cc1	CH ₃	H
106	F	C1	O-C(=O)c1cc(S(=O)(=O)C)cc1	CH ₃	H
107	F	C1	OSO ₂ N(CH ₃) ₂	CH ₃	H
108	F	C1	OSO ₂ C ₆ H ₅	CH ₃	H
109	F	C1	OCH ₂ C≡CH	CH ₂ (CH ₂) ₂ F	H
110	F	C1	OCH ₂ C≡CH	CH ₂ SO ₂ CH ₃	H
111	F	C1	OCH ₂ C≡CH	CH ₂ CH ₂ OCH ₃	H
112	F	C1	OCH ₂ C≡CH	CH ₃	C ₂ H ₅
113	F	C1	OH	H	H
114 ¹	F	C1	OCH(CH ₃) ₂	CH ₃	H
115 ²	F	C1	OCH ₂ C≡CH	CH ₃	H
116 ²	F	C1	OCH(CH ₃) ₂	CH ₃	H
117 ³	F	C1	OCH ₂ C≡CH	CH ₃	H
118 ³	F	C1	OCH(CH ₃) ₂	CH ₃	H
119	F	C1	OCH(CH ₃) ₂	CH ₂ OCH ₃	H
120	F	C1	OCH(CH ₃) ₂	CH ₃	H
121	F	OCH ₃	OCH(CH ₃) ₂	CH ₃	H
122	F	C1	O-CH ₂ -c1ccccc1	CH ₃	H
123	F	C1	O-C(=O)c1ccccc1	CH ₃	H
124	F	C1	OCH ₂ SCH ₃	CH ₃	H
125	F	C1	OCH ₂ CH=CH ₂	CH ₃	H
126	F	C1	OCH ₂ C(C1)=CH ₂	CH ₃	H
127	F	C1	O-CO-CH ₃	CH ₃	H
128	F	C1	OCH ₂ CO ₂ H	CH ₃	H

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Table 1
Representative Compounds

<u>Compound Number</u>	<u>X¹</u>	<u>X²</u>	<u>Z</u>	<u>R¹</u>	<u>R²</u>
129	F	C1	OCH ₂ CO ₂ CH ₃	CH ₃	H
130	F	C1	OCH ₂ CO ₂ CH ₂	CH ₃	H
131	F	C1	OCH ₂ CO ₂ CH ₂	CH ₃	H
132	F	C1	OCH ₂ CO ₂ CH ₂	CH ₃	H
133	F	C1	OCH ₂ CO ₂	CH ₃	H
134	F	C1	OCH ₂ CO ₂	CH ₃	H
135	F	C1	OCH ₂ CO ₂	CH ₃	H
136	F	C1	OCH ₂ CO ₂	CH ₃	H
137	F	C1	OCH ₂ CO ₂ -CH(CH ₂) ₅ CH ₂	CH ₃	H
138	F	C1	OCH ₂ CO-NH-CH ₂ OCH ₃	CH ₃	H
139	F	C1	OCH ₂ CO-NH-CH ₂ SCH ₃	CH ₃	H
140	F	C1	OCH ₂ CO ₂ CH ₂ CF ₃	CH ₃	H
141	F	C1	OCH(CH ₃)CO ₂ CH ₂ - CHCl ₂	CH ₃	H
142	F	C1	OC(CH ₃) ₂ CO ₂ CH ₂ - CH=CH ₂	CH ₃	H
143	F	C1	OCH ₂ CO ₂	CH ₃	H
144	F	C1	OCH ₂ CO ₂ CH ₂	CH ₃	H

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Table 1
Representative Compounds

Compound Number	X ¹	X ²	Z	R ¹	R ²
145	F	C1	OCH ₂ CO ₂ C ₆ H ₅	CH ₃	H
146	F	C1	OCH ₂ CO ₂ CH ₂ C ₆ H ₅	CH ₃	H
147	F	C1	OCH(CH ₃)CO ₂ CH ₂ CN	CH ₃	H
148	F	C1	OCH ₂ CO ₂ CH ₂ C≡CH	CH ₃	H
149	F	C1	OCH ₂ CO ₂ N=C(CH ₃) ₂	CH ₃	H
150	F	C1	OCH ₂ CO ₂ N=CH-C ₆ H ₅	CH ₃	H
151	F	C1	OCH ₂ CO ₂ N=C-C ₆ H ₅	CH ₃	H
152	F	C1	OCH ₂ CO ₂ N=C-C ₆ H ₅	H	H
153 ¹	F	C1	OCH(CH ₃) ₂	H	H
154 ²	F	C1	OCH(CH ₃) ₂	H	H
155 ³	F	C1	OCH(CH ₃) ₂	H	H
156 ¹	F	C1	OCH ₂ C≡CH	H	H
157 ²	F	C1	OCH ₂ C≡CH	H	H
158 ³	F	C1	OCH ₂ C≡CH	H	H
159 ¹	F	C1	OH	H	H
160 ²	F	C1	OH	H	H
161 ³	F	C1	OH	H	H
162 ¹	F	C1	OH	CH ₃	H
163 ²	F	C1	OH	CH ₃	H
164 ³	F	C1	OH	CH ₃	H
165 ¹	F	C1	OCH(CH ₃) ₂	H	CO ₂ H
166 ²	F	C1	OCH(CH ₃) ₂	H	CO ₂ H
167 ³	F	C1	OCH(CH ₃) ₂	H	CO ₂ H
168 ¹	F	C1	OCH ₂ C≡CH	H	CO ₂ H
169 ²	F	C1	OCH ₂ C≡CH	H	CO ₂ H
170 ³	F	C1	OCH ₂ C≡CH	H	CO ₂ H

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Table 1
Representative Compounds

Compound Number	X ¹	X ²	Z	R ¹	R ²
171 ¹	F	C1	OCH(CH ₃) ₂	CH ₃	CO ₂ H
172 ²	F	C1	OCH(CH ₃) ₂	CH ₃	CO ₂ H
173 ³	F	C1	OCH(CH ₃) ₂	CH ₃	CO ₂ H
174 ¹	F	C1	OCH ₂ C≡CH	CH ₃	CO ₂ H
175 ²	F	C1	OCH ₂ C≡CH	CH ₃	CO ₂ H
176 ³	F	C1	OCH ₂ C≡CH	CH ₃	CO ₂ H
177	F	C1	OCH ₂ C≡CH	H	H
178	F	C1	OCH(CH ₃) ₂	H	CO ₂ H
179	F	C1	OCH ₂ C≡CH	H	CO ₂ H
180	F	C1	OCH(CH ₃) ₂	CH ₃	CO ₂ H
181	F	C1	OCH ₂ C≡CH	CH ₃	CO ₂ H
182 ¹	F	C1	OCH(CH ₃) ₂	CH ₃	H
183	F	C1	OCH(CH ₃) ₂	CH ₂ CH ₂ CH ₃	H
184	F	C1	OCH(CH ₃) ₂	CH ₂ CH ₂ F	H
185	F	C1	OCH(CH ₃) ₂	CH ₂ (CH ₂) ₂ CH ₃	H
186	C1	C1	NH ₂	CH ₃	H
187	C1	C1	N(COCH ₃) ₂	CH ₃	H
188	C1	C1	C1	CH ₃	H
189	F	C1	I	CH ₃	H
190	F	C1	C1	CH ₃	H
191	F	C1	OCSN(CH ₂ CH ₃) ₂	CH ₃	H
192	F	C1	SCON(CH ₂ CH ₃) ₂	CH ₃	H
193	F	C1	OCH(CH ₃)CO ₂ C(CH ₃) ₃	CH ₃	H
194	F	C1	NHN=C(CH ₃) ₂	CH ₃	H
195	F	C1	OCH ₂ OCH ₂ CH ₂ OCH ₃	CH ₃	H
196	F	C1	OCH(CH ₃) ₂	CH ₂ SCH ₃	H
197	F	C1	OCH(CH ₃) ₂	CH ₂ SOCH ₃	H
198	F	C1	OCH(CH ₃)CO ₂ H	CH ₃	H
199 ¹	F	Br	OCH(CH ₃) ₂	CH ₃	H
200	F	C1	O(CH ₂) ₂ CH ₃	CH ₃	H

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Table 1
Representative Compounds

Compound Number	X ¹	X ²	Z	R ¹	R ²
201	F	Cl	O(CH ₂) ₂ CH=CH ₂	CH ₃	H
202	F	Cl	OCH ₂ CN	CH ₃	H
203 ¹	F	Br	OCH ₂ C≡CH	CH ₃	H
204 ²	F	Br	OCH ₂ C≡CH	CH ₃	H
205 ³	F	Br	OCH ₂ C≡CH	CH ₃	H
206	F	Cl	NHCH(CH ₂) ₄ CH	CH ₃	H
207	F	Cl	OCH(CH ₃)CO ₂ CH(CH ₃) ₂	CH ₃	H
208	F	Cl	OCH(CH ₃)CO-SC ₂ H ₅	CH ₃	H
209	F	Cl	OCHC(=O)NSO ₂ -C ₆ H ₄ -Cl CH ₃	CH ₃	H
210	F	Cl	OCHC(=O)NSO ₂ -C ₆ H ₄ -Cl CH ₃	CH ₃	H
211	F	Cl	OCH ₃	CH ₃	H
212	F	Cl	OCH ₂ SOCH ₃	CH ₃	H
213	F	Cl	OCH ₂ SO ₂ CH ₃	CH ₃	H
214	F	Cl	F	H	H
215	F	Cl	F	CH ₃	H
216 ²	F	Br	OCH(CH ₃) ₂	CH ₃	H
217 ³	F	Br	OCH(CH ₃) ₂	CH ₃	H
218	F	Cl	SO ₂ Cl	CH ₃	H
219	F	Cl	OCHC(=O)-S-C ₆ H ₄ -Cl CH ₃	CH ₃	H
220	F	Cl	OCH(O ₂ C ₂ H ₅)CO ₂ C ₂ H ₅	CH ₃	H
221	F	Cl	OCH(OCH ₃)CO ₂ CH ₃	CH ₃	H
222	F	Cl	SCHC(=O)NSO ₂ -C ₆ H ₄ -Cl CH ₃	CH ₃	H

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Table 1
Representative Compounds

<u>Compound Number</u>	<u>X¹</u>	<u>X²</u>	<u>Z</u>	<u>R¹</u>	<u>R²</u>
223	F	Cl	SCH(CH ₃)CO ₂ CH(CH ₃) ₂	CH ₃	H
224	F	Cl	SCH(CH ₂) ₃ CH	CH ₃	H
225	F	Cl	SCH ₂ OCH ₃	CH ₃	H
226	F	Cl	SCH ₂ CN	CH ₃	H
227	F	Br	OCH ₂ C≡CH	CH ₃	H
228	F	Cl	OCHCNHSO ₂ CH ₃ —————— O —————— OCH ₃	CH ₃	H
229	F	Cl	OCH ₂ Si(CH ₃) ₃	CH ₃	H
230	F	Cl	OC ₂ H ₅	CH ₃	H
231	F	Cl	OCHCNHSO ₂ CH ₃ —————— O —————— CO ₂ CH ₃	CH ₃	H
232	F	Cl	NHCH(CH ₃)CO ₂ C ₂ H ₅	CH ₃	H
233	F	Br	OCH(CH ₃)CO ₂ CH(CH ₃) ₂	CH ₃	H
234	F	Br	OCH ₂ OCH ₃	CH ₃	H
235	F	Br	OCHCNHSO ₂ CH ₃ —————— O —————— Cl	CH ₃	H
236	F	Cl	O(CH ₂) ₂ F	CH ₃	H
237	F	Cl	OCH ₂ CF ₃	CH ₃	H
238	F	Cl	SCH ₂ —————— O	CH ₃	H

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Table 1
Representative Compounds

Compound Number	X ¹	X ²	Z	R ¹	R ²
239	F	Cl	OCH ₂ C≡CH	CHF ₃	H
240	F	Br	H	CH ₃	H
241 ¹	F	Br	H	CH ₃	H
242 ²	F	Cl	H	CH ₃	H
243	F	Cl	OC(CH ₃) ₂ CO ₂ C ₂ H ₅	CH ₃	H
244	F	Cl	OCH ₂ -S-	CH ₃	H
245	F	Cl	CN	CH ₃	H
246	F	Cl	CH ₃	CH ₃	H
247	F	Cl	CF ₃	CH ₃	H
248	F	Cl	CO ₂ Na	CH ₃	H
249	F	Cl	SO ₃ Na	CH ₃	H
250	F	Br	OCH(CH ₃)CO ₂ Na	CH ₃	H

-
1. W¹ = O, W² = S
 2. W¹ = S, W² = O
 3. W¹ = W² = S
 4. X¹ = 3-Cl

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TABLE 2
Characterizing Data

Compound Number	M.P.(°C)	Empirical Formula	Elemental Analysis		
			C	H	N
1	79-81	C ₁₀ H ₉ N ₃ O ₂			
2	oil	C ₁₀ H ₈ FN ₃ O ₂ /0.25 H ₂ O	C F	53.22 53.55	3.80 3.48
3	99-100	C ₁₂ H ₁₀ ClN ₃ O ₂	C F	54.66 54.63	3.82 3.57
4	197(d)	C ₁₀ H ₇ Cl ₂ N ₃ O ₂			
5	109-110	C ₁₁ H ₉ Cl ₂ N ₃ O ₂			
6	202-203	C ₉ H ₅ ClFN ₃ O ₂			
7	114-116	C ₁₀ H ₇ ClFN ₃ O ₂			
8	167-168	C ₁₀ H ₇ Cl ₂ N ₃ O ₂	C F	44.14 43.85	2.59 2.40
9	199-201	C ₁₀ H ₇ Cl ₂ N ₃ O ₃			
10	163-164	C ₁₃ H ₁₃ Cl ₂ N ₃ O ₃	C F	47.29 47.47	3.97 3.82
11	195-197(d)	C ₁₃ H ₁₁ Cl ₂ N ₃ O ₅ /0.5 H ₂ O	C F	42.30 42.38	3.28 3.31
12	111-112	C ₁₃ H ₁₃ Cl ₂ N ₃ O ₃	C F	47.29 47.18	3.97 4.03
13	oily solid	C ₁₄ H ₁₅ Cl ₂ N ₃ O ₃			
14	230(d)	C ₁₄ H ₁₃ Cl ₂ N ₃ O ₃			
15	103-104	C ₁₅ H ₁₅ Cl ₂ N ₃ O ₃	C F	50.58 50.30	4.24 4.25
16	74-75	C ₁₆ H ₁₇ Cl ₂ N ₃ O ₃			
17	oil	C ₁₂ H ₁₁ ClFN ₃ O ₃			
18	82-84	C ₁₃ H ₁₃ ClFN ₃ O ₃			
19	84-86	C ₁₅ H ₁₅ ClFN ₃ O ₃			

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TABLE 2 (Continued)

Compound Number	M.P.(°C)	Empirical Formula	Elemental Analysis			
			C	H	N	
20	119-120	C ₁₃ H ₉ Cl ₂ N ₃ O ₃				
21	122-123	C ₁₃ H ₉ ClFN ₃ O ₃				
22	115-117	C ₁₄ H ₁₃ Cl ₂ N ₃ O ₅				
23	oil	C ₁₁ H ₉ Cl ₂ N ₃ O ₅ S	C F	36.08 36.99	2.48 2.70	11.48 10.85
24	134-135	C ₁₃ H ₉ ClFN ₃ O ₃ S				
25	142-144	C ₁₅ H ₁₃ Cl ₂ N ₃ O ₂	C F	50.87 50.37	3.70 3.95	11.86 11.66
26	oil	C ₁₃ H ₁₄ Cl ₂ FN ₃ O ₃	C F	46.43 46.45	3.90 3.66	11.60 11.48
27	108-110	C ₁₅ H ₁₅ Cl ₂ N ₃ O ₅	C F	46.41 46.14	3.89 3.70	10.82 10.65
28	169-170	C ₁₂ H ₈ Cl ₂ N ₄ O ₃	C F	43.46 43.27	2.58 2.36	16.95 16.69
29	82-83	C ₁₄ H ₁₅ Cl ₂ N ₃ O ₃	C F	48.86 49.25	4.39 4.22	12.21 12.15
30	183(d)	C ₁₀ H ₇ ClFN ₃ O ₃				
31	155(d)	C ₁₀ H ₆ ClN ₃ O ₄				
32	157(d)	C ₁₁ H ₈ ClN ₃ O ₅	C F	48.34 48.32	2.70 2.81	18.79 18.51
33	229-230	C ₉ H ₆ ClN ₃ O ₂	C F	57.82 58.11	4.61 4.50	20.23 19.73
34	200-202	C ₁₀ H ₉ N ₃ O ₂ /0.25 H ₂ O	C F	60.82 61.35	5.10 5.40	19.34 19.85
35	136-137	C ₁₁ H ₁₁ N ₃ O ₂	C F	50.54 50.70	3.39 3.66	17.68 17.92
36	152-154	C ₁₀ H ₈ ClN ₃ O ₂	C F	43.48 43.61	3.83 3.28	15.22 13.10

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TABLE 2 (Continued)

Compound Number	M.P.(°C)	Empirical Formula	Elemental Analysis		
			C	H	N
37	170-173	$C_{10}H_8ClN_3O_3/H_2O$	C F	50.63 50.12	4.67 3.85
					17.71 16.14
38	192(d)	$C_{10}H_9N_3O_3/H_2O$	C F	48.54 48.47	3.89 3.71
					15.44 14.10
39	108-110	$C_{11}H_{10}ClN_3O_3/0.25 H_2O$	C F	56.65 56.26	4.75 4.55
					18.01 17.66
40	114-116	$C_{11}H_{11}N_3O_3$	C F	47.07 47.20	3.65 3.77
					12.67 12.22
41	111-113	$C_{13}H_{12}ClF_2N_3O_3$	C F	47.01 46.51	3.66 3.69
					11.75 11.31
42	100-102	$C_{14}H_{13}ClFN_3O_5$			
43	oil	$C_{14}H_{13}ClFN_3O_5$			
44	oil	$C_{13}H_8ClF_2N_3O_3$	C F	47.65 48.10	2.46 2.58
					12.82 12.03
45	oil	$C_{14}H_{12}ClFN_4O_3$	C F	49.64 49.44	3.57 3.90
					16.54 14.65
46	132-134	$C_{10}H_6ClFN_4O_4$	C F	39.95 40.22	2.01 1.98
					18.64 18.51
47	150-152	$C_{10}H_8ClFN_4O_2$	C F	44.38 44.30	2.98 3.29
					20.70 20.40
48	127-129	$C_{13}H_8BrClFN_3O_3$			
49	208(d)	$C_{12}H_{10}ClFN_4O_4$			
50	70-71	$C_{15}H_{16}ClF_2N_3O_3$	C F	50.08 50.26	4.48 4.45
					11.68 12.00
53	89-92	$C_{13}H_{13}BrFN_3O_3$	C F	43.59 43.47	3.66 3.40
					11.73 11.72
55	oil	$C_{14}H_{16}FN_3O_3$			
74	oil	$C_{14}H_8ClFN_4O_3$			

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TABLE 2 (Continued)

Compound Number	M.P.(°C)	Empirical Formula	Elemental Analysis			
			C	H	N	
75	194-197	C ₁₇ H ₂₁ ClFN ₅ O ₃				
76	155-156	C ₁₇ H ₂₀ ClFN ₄ O ₄	C F	51.20 51.20	5.05 5.19	14.05 14.22
77	138-139	C ₁₁ H ₉ ClFN ₃ O ₂	C F	40.99 40.88	3.36 2.90	15.58 13.65
78	122-123	C ₁₅ H ₁₅ ClFN ₃ O ₃				
82	128-131	C ₁₁ H ₉ ClFN ₃ O ₂ S				
85	95-97	C ₁₃ H ₁₃ ClFN ₃ O ₂ S				
86	foam	C ₁₃ H ₉ ClFN ₃ O ₂ S				
89	solid	C ₁₃ H ₁₄ ClFN ₄ O ₂	C F	49.93 50.55	4.51 4.55	17.92 17.31
96	109-111	C ₁₂ H ₁₁ ClFN ₃ O ₄	C F	45.66 45.45	3.51 3.35	13.31 12.92
113	>225	C ₉ H ₅ ClFN ₃ O ₃	C F	41.96 43.20	1.96 2.54	16.31 14.69
114	80-81	C ₁₃ H ₁₂ ClFN ₃ O ₂ S	C F	47.35 47.71	3.97 4.05	12.74 12.69
119	100-102	C ₁₄ H ₁₅ ClFN ₃ O ₄	C F	48.92 49.09	4.40 4.32	12.22 11.95
124	oil	C ₁₂ H ₁₁ ClFN ₃ O ₃ S	C F	43.46 43.89	3.34 3.46	12.67 12.12
125	oil	C ₁₃ H ₁₁ ClFN ₃ O ₃	C F	50.09 50.16	3.56 3.73	13.48 13.00
182	134-135	C ₁₃ H ₉ ClFN ₃ O ₂ S				
183	61-63	C ₁₅ H ₁₇ ClFN ₃ O ₃	C F	52.72 52.55	5.01 4.95	12.29 11.53
184	oil	C ₁₄ H ₁₄ ClF ₂ N ₃ O ₃	C F	48.64 47.88	4.08 3.81	12.15 11.68

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TABLE 2 (Continued)

Compound Number	M.P.(°C)	Empirical Formula	Elemental Analysis			
			C	H	N	
185	73-74	C ₁₆ H ₁₉ ClFN ₃ O ₃	C F	54.01 54.55	5.38 5.59	11.81 11.40
186	168-171	C ₁₀ H ₈ Cl ₂ N ₄ O ₂				
187	foam	C ₁₄ H ₁₂ Cl ₂ N ₄ O ₄ / 0.5 H ₂ O	C F	44.23 44.15	3.45 3.15	14.73 14.44
188	172-173	C ₁₀ H ₆ Cl ₃ N ₃ O ₂	C F	39.18 39.83	1.97 2.35	13.71 13.55
189	182-185	C ₁₀ H ₆ ClFIN ₃ O ₂	C F	31.48 33.48	1.59 1.83	11.01 11.59
190	140-142	C ₁₀ H ₆ Cl ₂ FN ₃ O ₂	C F	41.41 41.65	2.08 2.13	14.49 14.05
191	120-121	C ₁₅ H ₁₆ ClFN ₄ O ₃ S	C F	46.57 46.47	4.17 4.02	14.48 14.29
192	156-157	C ₁₅ H ₁₆ ClFN ₄ O ₃ S	C F	46.57 46.66	4.17 4.14	14.48 14.37
193	86-88	C ₁₇ H ₁₉ ClFN ₃ O ₄	C F	50.94 51.13	5.03 4.75	10.48 10.35
194	146-147	C ₁₃ H ₁₃ ClFN ₅ O ₂	C F	47.94 48.20	4.02 3.77	21.50 21.46
195	oil	C ₁₄ H ₁₅ ClFN ₃ O ₅ / 0.5 H ₂ O	C F	45.60 45.67	4.37 4.07	11.39 11.20
196	95-97	C ₁₄ H ₁₅ ClFN ₃ O ₃ S	C F	46.73 46.76	4.20 4.24	11.68 11.39
197	138-140	C ₁₄ H ₁₅ ClFN ₃ O ₄ S	C F	44.74 44.15	4.02 3.78	11.18 10.99
198	123-125	C ₁₃ H ₁₁ ClFN ₃ O ₅	C F	45.43 45.14	3.23 3.23	12.23 11.95
200	88-89	C ₁₃ H ₁₃ ClFN ₃ O ₃	C F	49.77 49.74	4.18 4.07	13.39 13.34
201	oil	C ₁₄ H ₁₃ ClFN ₃ O ₃	C F	51.62 51.32	4.02 4.04	12.90 12.50

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TABLE 2 (Continued)

Compound Number	M.P.(°C)	Empirical Formula	Elemental Analysis		
			C	H	N
202	153-155	$C_{12}H_8ClFN_4O_3$	C	46.39	2.60
			F	46.08	2.49
206	gum	$C_{16}H_{18}ClFN_4O_2$	C	54.47	5.14
			F	55.83	4.80
207	oil	$C_{16}H_{17}ClFN_3O_5$	C	49.82	4.44
			F	47.82	4.31
208	oil	$C_{15}H_{15}ClFN_3O_4S$	C	44.75	4.02
			F	44.72	3.71
209	97(d)	$C_{19}H_{15}Cl_2FN_4O_6S/H_2O$	C	42.63	3.20
			F	42.61	4.06
210	solid	$C_{19}H_{15}Cl_2FN_4O_6S/H_2O$	C	42.63	3.20
			F	42.73	4.27
211	145-146	$C_{11}H_9ClFN_3O_3$	C	46.25	3.18
			F	45.90	2.80
212	164-166	$C_{12}H_{11}ClFN_3O_4S$	C	41.45	3.19
			F	41.45	3.07
213	154-156	$C_{12}H_{11}ClFN_3O_5S$	C	39.62	3.05
			F	39.30	3.15
214	233-234	$C_9H_4ClF_2N_3O_2$	C	41.64	1.55
			F	41.50	1.78
215	110-111	$C_{10}H_6ClF_2N_3O_2$	C	43.90	2.21
			F	43.64	2.13
218	123-125	$C_{10}H_6Cl_2FN_3O_4S$	C	33.92	1.71
			F	34.11	1.79
219	solid	$C_{19}H_{14}Cl_2FN_3O_4S$			
220	oil	$C_{16}H_{17}ClFN_3O_6$	C	47.83	4.27
			F	47.93	4.13
221	oil	$C_{14}H_{13}ClFN_3O_6$			
222	110(d)	$C_{19}H_{15}Cl_2FN_4O_5S_2$			

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TABLE 2 (Continued)

Compound Number	M.P.(°C)	Empirical Formula	Elemental Analysis		
			C	H	N
223	oil	C ₁₆ H ₁₇ ClFN ₃ O ₄ S	C F	47.82 46.14	4.26 4.10
					10.46 10.04
224	51-53	C ₁₅ H ₁₅ ClFN ₃ O ₂ S			
225	95-98	C ₁₂ H ₁₁ ClFN ₃ O ₂ S			
226	123-125	C ₁₂ H ₈ ClFN ₄ O ₂ S			
227	123-124	C ₁₃ H ₉ BrFN ₃ O ₃	C F	44.09 44.40	2.56 2.35
					11.87 11.42
228	195-196	C ₂₀ H ₁₈ ClFN ₄ O ₇ S	C F	46.83 46.94	3.53 3.80
					10.92 10.39
229	125-126	C ₁₄ H ₁₇ ClFN ₃ O ₃ Si	C F	46.99 47.26	4.79 4.62
					11.74 11.65
230	solid	C ₁₂ H ₁₁ ClFN ₃ O ₃			
231	solid	C ₂₁ H ₁₈ ClFN ₄ O ₈ S	C F	46.72 44.35	3.17 3.72
					10.38 7.43
232	oil	C ₁₅ H ₁₆ ClFN ₄ O ₄ /1.5 H ₂ O	C F	45.29 45.40	4.81 4.63
					14.08 13.65
233	gum	C ₁₆ H ₁₇ BrFN ₃ O ₃	C F	44.67 44.35	3.98 3.93
					9.77 9.44
234	79-81	C ₁₂ H ₁₁ BrFN ₃ O ₄	C F	40.02 39.86	3.08 2.91
					11.68 11.29
235	120(d)	C ₁₉ H ₁₅ BrClFN ₄ O ₆ S/H ₂ O	C F	39.36 39.62	2.96 2.78
					9.66 8.49
236	134-136	C ₁₂ H ₁₀ ClF ₂ N ₃ O ₃	C F	45.37 44.88	3.17 2.86
					13.23 12.87
237	gum	C ₁₂ H ₈ ClF ₄ N ₃ O ₃	C F	40.75 40.51	2.28 2.26
					11.88 11.16

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Table 3
Preemergence Herbicidal Activity

Compound No.	1 8.0 %K	2 8.0 %C	3 8.0 %K	4 8.0 %C
Species				
Cotton	0	90	90	0
Soybean	0	90	90	0
Field Corn	0	70	100	0
Wheat	0	80	100	0
Field Bindweed	0	90	100	0
Morningglory	30	90	90	0
Velvetleaf	-	90	-	0
Barnyardgrass	0	90	100	0
Green Foxtail	0	100	-	0
Johnsongrass	30	80	100	0
Compound No.	5 8.0 %C	6 8.0 %C	7 8.0 %C	8 8.0 %K
Species				
Cotton	0	10	100	0
Soybean	0	50	100	0
Field Corn	0	50	100	0
Wheat	0	50	100	10
Field Bindweed	0	50	100	20
Morningglory	0	30	100	50
Velvetleaf	0	100	100	-
Barnyardgrass	0	20	100	80
Green Foxtail	0	90	100	-
Johnsongrass	0	80	100	90
Compound No.	9 8.0 %K	10 8.0 %K	11 8.0 %K	12 8.0 %K
Species				
Cotton	20	0	0	10
Soybean	0	0	0	100
Field Corn	0	0	0	70
Wheat	10	0	0	100
Field Bindweed	0	0	0	100
Morningglory	10	0	0	100
Velvetleaf	0	100	0	100
Barnyardgrass	10	0	0	100
Green Foxtail	-	100	0	100
Johnsongrass	10	0	0	100

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Table 3
Preemergence Herbicidal Activity

Compound No. Rate (kg/ha)	13 4.0	15 8.0	16 8.0	17 8.0
	%K	%K	%K	%K
Species				
Cotton	0	0	0	0
Soybean	40	10	0	10
Field Corn	60	0	0	33
Wheat	40	20	0	0
Field Bindweed	50	0	100	0
Morningglory	0	0	80	0
Velvetleaf	100	100	0	-
Barnyardgrass	100	30	0	0
Green Foxtail	-	100	95	-
Johnsongrass	100	30	0	0
Compound No. Rate (kg/ha)	18 8.0	19 8.0	20 8.0	21 2.0
	%C	%C	%C	%C
Species				
Cotton	100	80	100	100
Soybean	100	90	100	100
Field Corn	100	100	100	100
Wheat	100	100	100	100
Field Bindweed	100	100	100	100
Morningglory	100	100	100	100
Velvetleaf	100	-	100	100
Barnyardgrass	100	100	100	100
Green Foxtail	-	-	100	100
Johnsongrass	100	100	100	100
Compound No. Rate (kg/ha)	22 8.0	23 8.0	24 0.5	25 8.0
	%C	%C	%C	%C
Species				
Cotton	100	90	100	0
Soybean	100	90	100	0
Field Corn	90	100	100	0
Wheat	0	100	100	20
Field Bindweed	100	80	100	0
Morningglory	70	90	90	20
Velvetleaf	90	100	100	0
Barnyardgrass	90	100	100	80
Green Foxtail	90	100	100	90
Johnsongrass	80	100	100	80

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Table 3
Preemergence Herbicidal Activity

Compound No. Rate (kg/ha)	26	27	28	29
	8.0	4.0	4.0	8.0
	%C	%C	%C	%C
<u>Species</u>				
Cotton	20	90	50	60
Soybean	40	30	50	90
Field Corn	90	80	100	90
Wheat	90	30	70	60
Field Bindweed	70	100	10	90
Morningglory	50	40	50	70
Velvetleaf	100	100	100	100
Barnyardgrass	80	100	100	100
Green Foxtail	100	100	100	100
Johnsongrass	90	100	80	100
Compound No. Rate (kg/ha)	30	31	32	33
	8.0	8.0	8.0	8.0
	%C	%C	%C	%C
<u>Species</u>				
Cotton	100	0	0	40
Soybean	100	0	0	40
Field Corn	100	0	0	30
Wheat	100	0	0	0
Field Bindweed	100	0	0	0
Morningglory	100	0	0	0
Velvetleaf	100	0	0	0
Barnyardgrass	100	0	0	0
Green Foxtail	100	0	0	0
Johnsongrass	100	0	0	0
Compound No. Rate (kg/ha)	34	35	36	37
	8.0	8.0	4.0	8.0
	%C	%C	%C	%C
<u>Species</u>				
Cotton	0	90	90	0
Soybean	0	80	90	70
Field Corn	0	80	100	20
Wheat	0	70	100	0
Field Bindweed	0	40	100	0
Morningglory	0	80	100	0
Velvetleaf	0	100	100	0
Barnyardgrass	0	90	100	0
Green Foxtail	0	90	100	0
Johnsongrass	0	80	100	0

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Table 3
Preemergence Herbicidal Activity

Compound No.	38	39	40	41
Rate (kg/ha)	8.0	8.0	8.0	0.5
	%C	%C	%C	%C

Species

Cotton	0	20	90	50
Soybean	0	50	90	90
Field Corn	0	60	100	90
Wheat	0	10	90	100
Field Bindweed	0	0	90	80
Morningglory	0	90	80	90
Velvetleaf	0	90	100	100
Barnyardgrass	0	50	100	100
Green Foxtail	0	80	100	100
Johnsongrass	0	20	100	100

Compound No.	42	43	44	45
Rate (kg/ha)	1.0	1.0	0.5	4.0
	%C	%C	%C	%C

Species

Cotton	100	40	100	100
Soybean	100	70	100	100
Field Corn	30	60	100	100
Wheat	60	0	100	100
Field Bindweed	100	100	100	100
Morningglory	100	100	100	100
Velvetleaf	100	100	100	100
Barnyardgrass	100	100	100	100
Green Foxtail	100	100	100	100
Johnsongrass	100	90	100	100

Compound No.	46	47	48	49
Rate (kg/ha)	4.0	4.0	0.25	2.0
	%C	%C	%C	%C

Species

Cotton	10	10	0	100
Soybean	90	100	0	100
Field Corn	10	30	50	100
Wheat	10	30	0	20
Field Bindweed	0	20	0	100
Morningglory	10	40	0	100
Velvetleaf	100	100	100	100
Barnyardgrass	0	70	80	100
Green Foxtail	90	60	90	100
Johnsongrass	10	70	60	100

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Table 3
Preemergence Herbicidal Activity

Compound No. Rate (kg/ha)	50	53	55	73
	2.0	0.25	0.5	4.0
	%C	%C	%C	%C
Species				
Cotton	80	0	30	40
Soybean	50	10	20	50
Field Corn	90	95	90	40
Wheat	100	100	0	90
Field Bindweed	40	80	30	100
Morningglory	100	100	20	100
Velvetleaf	100	95	100	100
Barnyardgrass	100	100	30	100
Green Foxtail	100	100	40	100
Johnsongrass	100	95	20	90
Compound No. Rate (kg/ha)	75	76	77	78
	1.0	1.0	1.0	1.0
	%C	%C	%C	%C
Species				
Cotton	100	90	100	30
Soybean	100	80	100	100
Field Corn	100	100	100	80
Wheat	100	90	90	70
Field Bindweed	100	90	100	40
Morningglory	100	90	100	50
Velvetleaf	100	100	100	100
Barnyardgrass	100	90	100	100
Green Foxtail	100	100	100	100
Johnsongrass	100	100	100	100
Compound No. Rate (kg/ha)	82	85	86	89
	2.0	0.5	0.125	0.5
	%C	%C	%C	%C
Species				
Cotton	100	30	20	70
Soybean	100	30	20	80
Field Corn	100	90	90	95
Wheat	95	30	40	95
Field Bindweed	95	20	20	80
Morningglory	100	20	30	40
Velvetleaf	100	100	100	100
Barnyardgrass	100	80	95	95
Green Foxtail	100	95	90	100
Johnsongrass	100	40	60	100

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Table 3
Preemergence Herbicidal Activity

Compound No.	96	113	114	119
Rate (kg/ha)	0.5	8.0	1.0	0.5
	%C	%C	%C	%C

Species	Cotton	70	0	40	10
Soybean	70	50	80	50	
Field Corn	100	20	100	80	
Wheat	100	10	100	20	
Field Bindweed	100	10	70	20	
Morningglory	100	10	90	30	
Velvetleaf	100	20	100	100	
Barnyardgrass	100	60	100	40	
Green Foxtail	100	20	100	70	
Johnsongrass	90	30	100	70	

Compound No.	124	125	182	183
Rate (kg/ha)	0.5	1.0	0.5	0.5
	%C	%C	%C	%C

Species	Cotton	100	90	100	0
Soybean	100	100	100	100	0
Field Corn	100	100	100	100	20
Wheat	100	100	100	100	30
Field Bindweed	100	100	100	100	30
Morningglory	100	100	90	90	0
Velvetleaf	100	100	100	100	80
Barnyardgrass	100	100	100	100	80
Green Foxtail	100	100	100	100	90
Johnsongrass	100	100	100	100	90

Compound No.	184	185	186	187
Rate (kg/ha)	0.5	0.5	4.0	4.0
	%C	%C	%C	%C

Species	Cotton	10	10	10	30
Soybean	30	0	10	10	20
Field Corn	100	10	10	10	20
Wheat	60	0	0	0	20
Field Bindweed	30	0	0	0	0
Morningglory	30	10	0	0	20
Velvetleaf	90	10	80	80	40
Barnyardgrass	90	20	20	20	10
Green Foxtail	100	20	0	0	10
Johnsongrass	90	0	0	0	10

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Table 3
Preemergence Herbicidal Activity

Compound No.	188	189	190	191
Rate (kg/ha)	2.0	1.0	1.0	8.0
	%C	%C	%C	%C
<u>Species</u>				
Cotton	20	30	40	60
Soybean	10	30	30	60
Field Corn	20	40	90	70
Wheat	0	30	40	40
Field Bindweed	10	30	20	80
Morningglory	20	20	30	60
Velvetleaf	80	100	100	100
Barnyardgrass	0	100	100	100
Green Foxtail	100	100	100	100
Johnsongrass	30	90	100	100
Compound No.	192	193	194	195
Rate (kg/ha)	8.0	8.0	4.0	0.5
	%C	%C	%C	%C
<u>Species</u>				
Cotton	90	100	100	80
Soybean	60	100	100	70
Field Corn	100	100	100	100
Wheat	60	100	100	70
Field Bindweed	100	100	100	80
Morningglory	80	100	100	100
Velvetleaf	100	100	100	100
Barnyardgrass	100	100	100	100
Green Foxtail	100	100	100	100
Johnsongrass	100	100	100	90
Compound No.	196	197	198	200
Rate (kg/ha)	2.0	4.0	1.0	1.0
	%C	%C	%C	%C
<u>Species</u>				
Cotton	20	50	100	60
Soybean	20	50	95	50
Field Corn	90	100	50	100
Wheat	30	80	80	90
Field Bindweed	10	60	90	70
Morningglory	20	40	100	100
Velvetleaf	80	100	100	100
Barnyardgrass	100	50	100	100
Green Foxtail	100	90	100	100
Johnsongrass	90	90	95	100

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Table 3
Preemergence Herbicidal Activity

Compound No. Rate (kg/ha)	201	202	206	207
	1.0 %C	1.0 %C	4.0 %C	1.0 %C
Species				
Cotton	50	90	30	100
Soybean	50	90	70	100
Field Corn	100	90	95	70
Wheat	80	50	80	90
Field Bindweed	80	100	100	100
Morningglory	50	100	80	80
Velvetleaf	100	100	100	100
Barnyardgrass	100	100	80	100
Green Foxtail	100	100	100	100
Johnsongrass	90	90	100	100
Compound No. Rate (kg/ha)	208	209	210	211
	1.0 %C	1.0 %C	1.0 %C	2.0 %C
Species				
Cotton	100	95	100	100
Soybean	100	80	70	95
Field Corn	80	10	20	100
Wheat	80	30	60	100
Field Bindweed	100	100	100	100
Morningglory	100	100	95	100
Velvetleaf	100	100	100	100
Barnyardgrass	100	100	70	100
Green Foxtail	100	95	80	100
Johnsongrass	95	90	70	100
Compound No. Rate (kg/ha)	212	213	214	215
	2.0 %C	4.0 %C	8.0 %C	4.0 %C
Species				
Cotton	100	100	10	100
Soybean	100	100	50	100
Field Corn	100	100	50	100
Wheat	100	100	30	100
Field Bindweed	100	100	90	100
Morningglory	100	100	70	100
Velvetleaf	100	100	100	100
Barnyardgrass	100	100	20	100
Green Foxtail	100	100	100	100
Johnsongrass	100	100	60	100

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Table 3
Preemergence Herbicidal Activity

Compound No.	218	219	220	221
Rate (kg/ha)	8.0	1.0	2.0	2.0
Species	%C	%C	%C	%C
Cotton	20	20	30	70
Soybean	0	30	90	95
Field Corn	20	30	70	70
Wheat	10	20	0	30
Field Bindweed	50	30	30	100
Morningglory	20	50	95	100
Velvetleaf	100	100	80	80
Barnyardgrass	30	90	90	95
Green Foxtail	100	100	90	100
Johnsongrass	90	60	70	95
Compound No.	222	223	224	225
Rate (kg/ha)	1.0	1.0	1.0	0.25
Species	%C	%C	%C	%C
Cotton	70	100	30	10
Soybean	40	100	70	20
Field Corn	30	95	80	95
Wheat	10	70	20	90
Field Bindweed	90	90	20	80
Morningglory	100	100	90	100
Velvetleaf	100	100	100	100
Barnyardgrass	0	95	100	100
Green Foxtail	0	100	100	90
Johnsongrass	0	95	80	40
Compound No.	226	227	228	229
Rate (kg/ha)	2.0	0.125	0.5	4.0
Species	%C	%C	%C	%C
Cotton	100	50	90	20
Soybean	100	30	95	30
Field Corn	100	100	0	80
Wheat	100	100	30	50
Field Bindweed	90	95	100	80
Morningglory	100	70	100	95
Velvetleaf	100	100	100	100
Barnyardgrass	100	100	70	90
Green Foxtail	100	100	95	100
Johnsongrass	100	100	100	95

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Table 3
Preemergence Herbicidal Activity

Compound No. Rate (kg/ha)	230 2.0	231 0.5	232 2.0	233 0.5	234 0.125
	%C	%C	%C	%C	%C
<u>Species</u>					
Cotton	90	80	100	70	80
Soybean	95	70	100	95	10
Field Corn	100	10	40	40	95
Wheat	100	20	90	60	100
Field Bindweed	100	100	100	100	100
Morningglory	95	90	60	95	100
Velvetleaf	100	100	100	100	100
Barnyardgrass	100	20	70	100	100
Green Foxtail	100	30	100	100	100
Johnsongrass	100	70	30	80	100

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Table 4
Postemergence Herbicidal Activity

Compound No.	1	2	3	4
Rate (kg/ha)	8.0 %K	8.0 %C	8.0 %K	8.0 %C
Species				
Cotton	0	30	100	0
Soybean	0	40	0	20
Field Corn	0	30	30	0
Wheat	0	30	50	10
Field Bindweed	0	40	100	0
Morningglory	0	40	100	0
Velvetleaf	0	60	100	0
Barnyardgrass	0	0	30	30
Green Foxtail	0	20	100	0
Johnsongrass	0	0	100	0
 Compound No.				
5				
Rate (kg/ha)	8.0 %C	8.0 %C	8.0 %C	8.0 %K
Species				
Cotton	20	60	100	0
Soybean	20	60	100	0
Field Corn	0	70	100	0
Wheat	20	20	100	0
Field Bindweed	0	30	100	0
Morningglory	0	30	100	0
Velvetleaf	0	60	100	0
Barnyardgrass	0	20	100	100
Green Foxtail	0	100	100	-
Johnsongrass	0	40	100	100
 Compound No.				
9				
Rate (kg/ha)	8.0 %K	8.0 %K	8.0 %K	8.0 %K
Species				
Cotton	0	20	0	100
Soybean	0	0	0	100
Field Corn	0	0	0	100
Wheat	0	0	0	100
Field Bindweed	0	0	10	100
Morningglory	0	20	0	100
Velvetleaf	0	100	0	100
Barnyardgrass	0	0	0	100
Green Foxtail	0	0	0	100
Johnsongrass	0	0	10	100

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Table 4
Postemergence Herbicidal Activity

Compound No. Rate (kg/ha)	13 4.0	15 8.0	16 8.0	17 8.0
	%K	%K	%K	%K
<u>Species</u>				
Cotton	70	95	20	0
Soybean	0	0	0	0
Field Corn	30	0	30	30
Wheat	0	0	0	0
Field Bindweed	70	0	70	70
Morningglory	20	60	10	10
Velvetleaf	100	100	100	100
Barnyardgrass	0	20	20	20
Green Foxtail	-	100	100	100
Johnsongrass	90	60	100	100
 <u>Compound No.</u>				
Rate (kg/ha)	18 8.0	19 8.0	20 8.0	21 0.25
	%K	%K	%K	%C
<u>Species</u>				
Cotton	100	100	100	100
Soybean	100	100	100	70
Field Corn	100	100	100	100
Wheat	100	100	100	100
Field Bindweed	100	100	100	100
Morningglory	100	100	100	100
Velvetleaf	100	100	100	100
Barnyardgrass	100	100	100	100
Green Foxtail	100	100	100	100
Johnsongrass	100	100	100	100
 <u>Compound No.</u>				
Rate (kg/ha)	22 8.0	23 8.0	24 0.5	25 8.0
	%C	%C	%C	%C
<u>Species</u>				
Cotton	100	80	100	30
Soybean	90	100	80	40
Field Corn	70	100	90	0
Wheat	20	90	80	40
Field Bindweed	90	50	100	0
Morningglory	90	70	100	10
Velvetleaf	100	100	100	50
Barnyardgrass	100	100	100	30
Green Foxtail	100	100	100	100
Johnsongrass	30	100	100	30

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Table 4
Postemergence Herbicidal Activity

Compound No.	26	27	28	29
Rate (kg/ha)	8.0	8.0	8.0	8.0
Species	%C	%C	%C	%C
Cotton	90	100	80	100
Soybean	60	90	90	70
Field Corn	90	70	100	100
Wheat	100	100	40	100
Field Bindweed	60	100	50	100
Morningglory	50	80	80	100
Velvetleaf	100	100	90	100
Barnyardgrass	90	100	100	100
Green Foxtail	100	100	100	100
Johnsongrass	90	100	70	100

Compound No.	30	31	32	33
Rate (kg/ha)	8.0	8.0	8.0	8.0
Species	%C	%C	%C	%C
Cotton	100	10	10	10
Soybean	90	20	10	30
Field Corn	100	20	20	20
Wheat	80	20	10	20
Field Bindweed	100	0	10	20
Morningglory	100	10	10	30
Velvetleaf	100	0	10	20
Barnyardgrass	100	30	20	20
Green Foxtail	100	20	10	20
Johnsongrass	100	30	20	20

Compound No.	34	35	36	37
Rate (kg/ha)	8.0	8.0	8.0	8.0
Species	%C	%C	%C	%C
Cotton	20	90	90	0
Soybean	10	80	90	0
Field Corn	20	10	90	0
Wheat	20	30	30	0
Field Bindweed	10	30	100	0
Morningglory	20	10	100	10
Velvetleaf	20	100	100	0
Barnyardgrass	30	30	80	0
Green Foxtail	10	80	100	50
Johnsongrass	20	30	80	0

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Table 4
Postemergence Herbicidal Activity

Compound No.	38	39	40	41
Rate (kg/ha)	8.0	8.0	8.0	0.5
Species	%C	%C	%C	%C
Cotton	10	30	60	100
Soybean	10	40	60	70
Field Corn	20	30	30	80
Wheat	10	30	30	70
Field Bindweed	10	30	40	100
Morningglory	10	20	60	100
Velvetleaf	0	60	80	100
Barnyardgrass	10	40	30	80
Green Foxtail	30	70	90	100
Johnsongrass	0	50	50	90
Compound No.	42	43	44	45
Rate (kg/ha)	1.0	1.0	0.5	4.0
Species	%C	%C	%C	%C
Cotton	100	100	100	100
Soybean	100	90	100	90
Field Corn	70	80	100	100
Wheat	100	20	100	100
Field Bindweed	100	100	100	100
Morningglory	100	90	100	100
Velvetleaf	100	100	100	100
Barnyardgrass	100	100	100	100
Green Foxtail	100	100	100	100
Johnsongrass	100	60	100	100
Compound No.	46	47	48	49
Rate (kg/ha)	4.0	4.0	0.25	2.0
Species	%C	%C	%C	%C
Cotton	10	90	50	100
Soybean	10	90	30	100
Field Corn	0	10	0	100
Wheat	0	10	0	10
Field Bindweed	10	50	10	90
Morningglory	40	30	10	90
Velvetleaf	0	90	90	100
Barnyardgrass	10	0	0	100
Green Foxtail	50	90	20	100
Johnsongrass	20	0	0	50

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Table 4
Postemergence Herbicidal Activity

Compound No.	50	53	55	73
Rate (kg/ha)	2.0	0.25	0.5	4.0
	%C	%C	%C	%C
Species				
Cotton	80	90	40	80
Soybean	50	80	30	50
Field Corn	100	90	10	40
Wheat	70	40	20	80
Field Bindweed	80	80	20	80
Morningglory	20	80	40	80
Velvetleaf	100	100	80	100
Barnyardgrass	90	90	10	20
Green Foxtail	100	100	30	90
Johnsongrass	90	60	0	80
Compound No.	75	76	77	78
Rate (kg/ha)	1.0	1.0	4.0	1.0
	%C	%C	%C	%C
Species				
Cotton	100	90	100	100
Soybean	100	90	90	60
Field Corn	80	40	80	20
Wheat	70	30	50	40
Field Bindweed	100	100	100	80
Morningglory	100	90	100	80
Velvetleaf	100	100	100	100
Barnyardgrass	80	30	100	50
Green Foxtail	100	80	100	50
Johnsongrass	80	50	80	40
Compound No.	82	85	86	89
Rate (kg/ha)	2.0	0.5	0.125	0.5
	%C	%C	%C	%C
Species				
Cotton	95	95	95	80
Soybean	95	90	70	90
Field Corn	100	80	90	95
Wheat	90	50	70	80
Field Bindweed	100	95	95	70
Morningglory	90	80	100	60
Velvetleaf	100	100	100	100
Barnyardgrass	100	70	90	90
Green Foxtail	100	100	100	90
Johnsongrass	80	60	30	90

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Table 4
Postemergence Herbicidal Activity

Compound No. Rate (kg/ha)	96	113	114	119
	0.5	8.0	1.0	0.5
	%C	%C	%C	%C
<u>Species</u>				
Cotton	100	0	100	70
Soybean	90	20	90	30
Field Corn	100	20	100	20
Wheat	90	10	50	10
Field Bindweed	100	10	100	70
Morningglory	100	10	100	40
Velvetleaf	100	20	100	100
Barnyardgrass	100	20	100	30
Green Foxtail	100	10	100	40
Johnsongrass	90	10	70	30
Compound No. Rate (kg/ha)	124	125	182	183
	4.0	1.0	0.5	0.5
	%C	%C	%C	%C
<u>Species</u>				
Cotton	100	100	100	80
Soybean	100	80	80	60
Field Corn	100	100	90	100
Wheat	100	90	80	30
Field Bindweed	100	100	100	30
Morningglory	100	100	100	40
Velvetleaf	100	100	100	90
Barnyardgrass	100	100	100	10
Green Foxtail	100	100	100	90
Johnsongrass	100	80	100	30
Compound No. Rate (kg/ha)	184	185	186	187
	0.5	0.5	4.0	4.0
	%C	%C	%C	%C
<u>Species</u>				
Cotton	90	30	30	30
Soybean	60	10	20	10
Field Corn	100	30	10	20
Wheat	70	10	10	20
Field Bindweed	80	10	20	0
Morningglory	70	30	0	0
Velvetleaf	100	50	30	10
Barnyardgrass	50	10	20	0
Green Foxtail	100	30	0	0
Johnsongrass	80	0	0	0

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Table 4
Postemergence Herbicidal Activity

Compound No. Rate (kg/ha)	188	189	190	191
	2.0	1.0	1.0	8.0
	%C	%C	%C	%C
Species				
Cotton	30	80	80	80
Soybean	10	60	80	60
Field Corn	10	20	40	90
Wheat	20	20	20	50
Field Bindweed	30	30	50	30
Morningglory	10	70	90	70
Velvetleaf	100	100	100	100
Barnyardgrass	10	20	80	90
Green Foxtail	20	40	90	90
Johnsongrass	0	20	30	80
 Compound No.				
Rate (kg/ha)	192	193	194	195
	8.0	8.0	4.0	0.5
	%C	%C	%C	%C
Species				
Cotton	90	100	100	70
Soybean	50	100	80	30
Field Corn	90	100	100	30
Wheat	50	100	40	30
Field Bindweed	30	100	90	50
Morningglory	100	100	100	80
Velvetleaf	100	100	100	100
Barnyardgrass	100	100	90	90
Green Foxtail	100	100	80	100
Johnsongrass	100	100	30	80
 Compound No.				
Rate (kg/ha)	196	197	198	200
	2.0	4.0	1.0	1.0
	%C	%C	%C	%C
Species				
Cotton	90	90	100	100
Soybean	70	30	100	80
Field Corn	20	0	95	95
Wheat	0	0	100	90
Field Bindweed	60	0	100	100
Morningglory	30	0	100	100
Velvetleaf	100	100	100	100
Barnyardgrass	90	30	100	100
Green Foxtail	100	70	100	100
Johnsongrass	0	80	100	95

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Table 4
Postemergence Herbicidal Activity

Compound No.	201	202	206	207
Rate (kg/ha)	1.0	1.0	4.0	1.0
	%C	%C	%C	%C

Species

Cotton	95	100	90	100
Soybean	70	90	80	100
Field Corn	100	100	100	50
Wheat	70	40	40	90
Field Bindweed	100	100	95	100
Morningglory	100	100	90	90
Velvetleaf	100	100	100	100
Barnyardgrass	95	100	95	100
Green Foxtail	100	100	100	100
Johnsongrass	40	80	100	80

Compound No.	208	209	210	211
Rate (kg/ha)	1.0	1.0	1.0	2.0
	%C	%C	%C	%C

Species

Cotton	100	100	50	100
Soybean	100	90	20	95
Field Corn	20	20	10	100
Wheat	90	30	20	100
Field Bindweed	100	100	100	100
Morningglory	100	100	100	100
Velvetleaf	100	100	100	100
Barnyardgrass	100	100	95	100
Green Foxtail	100	100	95	100
Johnsongrass	70	70	60	100

Compound No.	212	213	214	215
Rate (kg/ha)	2.0	4.0	8.0	4.0
	%C	%C	%C	%C

Species

Cotton	100	100	30	100
Soybean	100	100	50	100
Field Corn	100	100	80	100
Wheat	100	100	30	100
Field Bindweed	100	100	90	100
Morningglory	100	100	100	100
Velvetleaf	100	100	100	100
Barnyardgrass	100	100	60	100
Green Foxtail	100	100	95	100
Johnsongrass	100	100	80	100

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Table 4
Postemergence Herbicidal Activity

Compound No. Rate (kg/ha)	218	219	220	221
	8.0	1.0	2.0	2.0
	%C	%C	%C	%C
Species				
Cotton	70	95	80	95
Soybean	60	60	100	95
Field Corn	30	70	90	95
Wheat	10	50	40	50
Field Bindweed	90	80	90	100
Morningglory	40	90	100	100
Velvetleaf	100	100	100	100
Barnyardgrass	0	70	100	100
Green Foxtail	90	95	100	100
Johnsongrass	0	30	50	100
Compound No. Rate (kg/ha)	222	223	224	225
	1.0	1.0	1.0	0.25
	%C	%C	%C	%C
Species				
Cotton	95	100	100	100
Soybean	80	100	80	80
Field Corn	40	40	40	60
Wheat	30	95	40	60
Field Bindweed	100	100	60	95
Morningglory	95	100	50	90
Velvetleaf	100	100	100	100
Barnyardgrass	0	100	10	60
Green Foxtail	60	100	40	90
Johnsongrass	0	100	10	40
Compound No. Rate (kg/ha)	226	227	228	229
	2.0	0.125	0.5	4.0
	%C	%C	%C	%C
Species				
Cotton	100	90	100	90
Soybean	95	60	100	60
Field Corn	100	90	30	30
Wheat	100	90	80	50
Field Bindweed	100	100	100	80
Morningglory	100	95	100	100
Velvetleaf	100	100	100	100
Barnyardgrass	100	100	100	90
Green Foxtail	100	100	95	95
Johnsongrass	100	95	95	70

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Table 4
Postemergence Herbicidal Activity

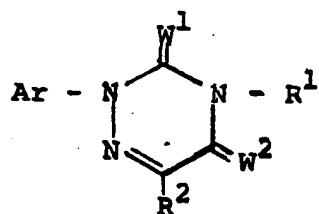
Compound No. Rate (kg/ha)	230 2.0	231 0.5	232 2.0	233 0.5	234 0.125
	%C	%C	%C	%C	%C
<u>Species</u>					
Cotton	100	40	100	95	70
Soybean	100	80	100	95	60
Field Corn	100	0	100	40	80
Wheat	100	50	100	80	70
Field Bindweed	100	100	100	100	70
Morningglory	100	100	100	80	80
Velvetleaf	100	100	100	95	100
Barnyardgrass	100	20	100	100	80
Green Foxtail	100	40	100	100	95
Johnsongrass	95	10	100	30	40

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Claims:

1. A method for controlling undesired plant growth which comprises applying to the locus where control is desired an herbicidally effective amount of an
- 5 herbicidal compound of the formula

10



where Ar is a dihalophenyl radical; W¹ and W² are
 15 independently selected from oxygen and sulfur; R¹ is alkyl of 1 to 6 carbon atoms, cyanoalkyl of 1 to 5 alkyl carbon atoms, haloalkyl of 1 to 5 carbon atoms, alkenyl or alkynyl of 2 to 5 carbon atoms, alkoxyalkyl, alkylthioalkyl, alkylsulfinylalkyl, or alkylsulfonyl-
 20 alkyl of 2 to 5 carbon atoms, or amino; and R² is hydrogen, alkyl of 1 to 4 carbon atoms, haloalkyl of 1 to 4 carbon atoms, alkenyl or alkynyl of 2 to 4 carbon atoms, alkoxyalkyl of 2 to 4 carbon atoms, amino, fluorine, chlorine, bromine, hydroxycarbonyl, or
 25 alcoxycarbonyl of 1 to 4 alkyl carbon atoms in admixture with a carrier suitable for the intended herbicidal use.

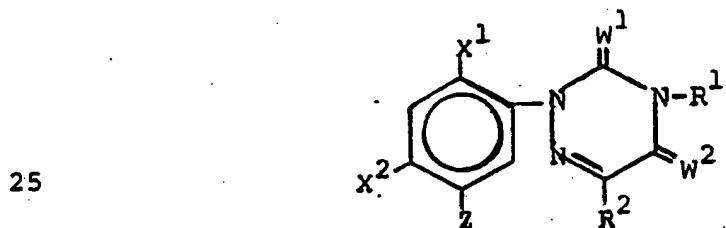
2. The method of claim 1 wherein the dihalophenyl
 30 radical is a 2,4-dihalophenyl radical.

3. The method of claim 2 wherein R¹ is methyl, fluoromethyl, or cyanomethyl and R² is hydrogen.

35 4. The method of claim 3 wherein the 2,4-dihalophenyl radical is a 5-(alkoxy of 1 to 6 carbon atoms)-2,4-dihalophenyl radical.

5. The method of claim 3 wherein the 2,4-dihalophenyl radical is a 5-(alkynyloxy of 2 to 5 carbon atoms)-2,4-dihalophenyl radical.
- 5 6. The method of claim 3 wherein the 2,4-dihalophenyl radical is a 5-(alkoxyalkoxy of 2 to 8 carbon atoms)-2,4-dihalophenyl radical.
- 10 7. The method of claim 3 wherein the 2,4-dihalophenyl radical is substituted at the C-5 position with a group of the formula $-Q-CH(CH_3)-CO-Q^1-R^5$ in which Q and Q^1 are independently O, S, or NH and R^5 is alkyl of 1 to 6 carbon atoms, or Q^1 and R^5 together form a phenylsulfonylamino group in which the phenyl is unsubstituted or substituted with fluorine, chlorine, bromine, alkyl of 1 to 4 carbon atoms, alkoxy of 1 to 4 carbon atoms, or alkoxy carbonyl of 1 to 4 alkyl carbon atoms.

20 8. A compound of the formula



wherein W^1 and W^2 are independently oxygen or
30 sulfur;
 R^1 is alkyl of 1 to 6 carbon atoms, haloalkyl of 1 to 5 carbon atoms, cyanoalkyl of 1 to 5 alkyl carbon atoms, alkenyl or alkynyl of 2 to 5 carbon atoms, alkoxyalkyl, alkylthioalkyl, alkylsulfinylalkyl, or
35 alkylsulfonylalkyl of 2 to 5 carbon atoms, or amino;
 R^2 is hydrogen or alkyl of 1 to 4 carbon atoms;

X^1 is fluorine or chlorine;

X^2 is fluorine, chlorine, bromine, alkyl of 1 to 6 carbon atoms, haloalkyl of 1 to 5 carbon atoms, or alkoxy of 1 to 6 carbon atoms;

5 Z is hydrogen, fluorine, chlorine, bromine, iodine, cyano, nitro, amino, alkoxy carbonyl amino of 1 to 6 alkyl carbon atoms, di(alkyl carbonyl) amino in which each alkyl is of 1 to 6 carbon atoms, hydroxysulfonyl, alkyl of 1 to 6 carbon atoms, haloalkyl of 1 to 5 carbon atoms, $-QR$, $-CO-R^6$, $-S(O)R^8$, $-Q^2R^9$, $-OSO_2R^{10}$,
10 $NHN=CR^{11}R^{12}$, or $-Q-CR^3R^4-CO-Q^1-R^5$;

Q and Q^1 are independently O, S, or NR^7 in which R^7 is hydrogen or alkyl of 1 to 6 carbon atoms;

Q^2 is O or S;

15 R is hydrogen, alkyl of 1 to 6 carbon atoms (which is unsubstituted or substituted with cycloalkyl of 3 to 7 carbon atoms), cycloalkyl of 3 to 7 carbon atoms (which is unsubstituted or substituted with alkyl of 1 to 6 carbon atoms), alkoxyalkyl of 2 to 8 carbon atoms,
20 alkoxyalkoxyalkyl of 3 to 8 carbon atoms, alkylthioalkyl, alkylsulfinylalkyl, or alkylsulfonylalkyl of 2 to 8 carbon atoms, tri(alkyl of 1 to 4 carbon atoms)-silyl(alkyl of 1 to 4 carbon atoms), cyanoalkyl of 1 to 5 alkyl carbon atoms, alkenyl or haloalkenyl of 2 to 5
25 carbon atoms, alkynyl or haloalkynyl of 2 to 5 carbon atoms, haloalkyl of 1 to 5 carbon atoms, alkylcarbonyl of 1 to 6 alkyl carbon atoms, or dialkylaminocarbonyl or dialkylaminothiocarbonyl in which each alkyl is of 1 to 6 carbon atoms;

30 R^3 is hydrogen or alkyl of 1 to 4 carbon atoms, and R^4 is hydrogen, alkyl of 1 to 4 carbon atoms, or alkoxy of 1 to 4 carbon atoms;

35 R^5 is hydrogen, alkyl of 1 to 6 carbon atoms (which is unsubstituted or substituted with cycloalkyl of 3 to 7 carbon atoms), cycloalkyl of 3 to 7 carbon atoms (which is unsubstituted or substituted with alkyl of 1 to 4 carbon atoms), alkoxyalkyl or alkylthioalkyl

of 2 to 6 carbon atoms, haloalkyl of 1 to 5 carbon atoms, alkenyl of 2 to 5 carbon atoms, cycloalkenyl of 5 to 7 carbon atoms (which is unsubstituted or substituted with alkyl of 1 to 4 carbon atoms), cycloalkenyl-

5 alkyl of 6 to 10 carbon atoms, phenyl or phenylmethyl (each of which is unsubstituted or ring-substituted with fluorine, chlorine, bromine, or alkyl, alkoxy or alkylthio of 1 to 4 carbon atoms), cyanoalkyl of 1 to 5 alkyl carbon atoms, alkynyl of 2 to 5 carbon atoms,

10 alkylimino of 1 to 6 carbon atoms (which is unsubstituted or substituted with cycloalkyl of 3 to 7 carbon atoms), or cycloalkylimino of 5 to 7 carbon atoms (which is unsubstituted or substituted with alkyl of 1 to 4 carbon atoms); or Q¹ and R⁵ together represent

15 a phenylsulfonylamino group in which the phenyl is unsubstituted or substituted with fluorine, chlorine, bromine, alkyl of 1 to 4 carbon atoms, alkoxy of 1 to 4 carbon atoms, or alkoxycarbonyl of 1 to 4 alkyl carbon atoms;

20 R⁶ is hydroxy, alkoxy or alkylthio of 1 to 6 carbon atoms, alkoxyalkoxy of 2 to 6 carbon atoms, amino, or alkylamino or dialkylamino wherein each alkyl is of 1 to 6 carbon atoms and is unsubstituted or substituted with alkoxy of 1 to 4 carbon atoms;

25 R⁸ is alkyl of 1 to 6 carbon atoms or alkenyl or alkynyl of 2 to 5 carbon atoms, and m is 1 or 2;

R⁹ is a 5- or 6-membered ring heterocyclic group of 1 or 2 same or different heteroatoms selected from O, S, and N or an alkyl radical of 1 to 5 carbon atoms

30 substituted with said heterocyclic group;

35 R¹⁰ is alkyl of 1 to 6 carbon atoms (which is unsubstituted or substituted with halogen, cyano, alkoxy or alkylthio of 1 to 4 carbon atoms, or alkylamino or dialkylamino in which alkyl is of 1 to 4 carbon atoms), phenyl, or alkylamino or dialkylamino in which alkyl is of 1 to 4 carbon atoms; and

R¹¹ is hydrogen or alkyl of 1 to 4 carbon atoms

and R^{12} is alkyl of 1 to 4 carbon atoms, or $C(R^{11})(R^{12})$ taken as a unit is cycloalkyl of 3 to 7 carbon atoms.

9. The compound of claim 8 wherein R^2 is hydrogen
5 or methyl.

10. The compound of claim 9 wherein X^1 is fluorine,
 X^2 is chlorine or bromine, and Z is hydrogen.

10 11. The compound of claim 10 wherein W^1 and W^2 are
both oxygen, R^1 is alkyl of 1 to 4 carbon atoms,
cyanoalkyl of 1 to 3 alkyl carbon atoms, fluoroalkyl of
1 to 3 carbon atoms, alkenyl or alkynyl of 3 to 5
carbon atoms, alkoxyalkyl of 2 to 4 carbon atoms,
15 alkylthioalkyl of 2 to 4 carbon atoms, alkylsulfinyl-
alkyl of 2 to 4 carbon atoms, or alkylsulfonylalkyl of
2 to 4 carbon atoms, and R^2 is hydrogen.

12. The compound of claim 11 in which R^1 is methyl,
20 ethyl, cyanomethyl, 2-propenyl, 2-propynyl, fluoro-
methyl having 1 or 2 fluorine atoms, 2-fluoroethyl,
3-fluoropropyl, methoxymethyl, methylthiomethyl,
methylsulfinylmethyl, or methylsulfonylmethyl.

25 13. The compound of claim 9 wherein Z is other than
hydrogen.

14. The compound of 13 wherein X^2 is chlorine or
bromine.

30 15. The compound of claim 14 wherein X^1 is fluorine.

16. The compound of claim 15 wherein W^1 and W^2 are
both oxygen.

35 17. The compound of claim 16 wherein R^2 is hydrogen.

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18. The compound of claim 17 wherein R¹ is alkyl of 1 to 4 carbon atoms, cyanoalkyl of 1 to 3 carbon atoms, fluoroalkyl of 1 to 3 carbon atoms, alkenyl or alkynyl of 3 to 5 carbon atoms, alkoxyalkyl of 2 to 4 carbon atoms, alkylthioalkyl of 2 to 4 carbon atoms, alkylsulfinylalkyl of 2 to 4 carbon atoms, or alkylsulfonylalkyl of 2 to 4 carbon atoms.
19. The compound of claim 18 wherein R¹ is methyl, ethyl, cyanomethyl, 2-propenyl, 2-propynyl, fluoromethyl having 1 or 2 fluorine atoms, 2-fluoroethyl, 3-fluoropropyl, methoxymethyl, methylthiomethyl, methylsulfinylmethyl, or methylsulfonylmethyl.
- 15 20. The compound of claim 19 wherein R¹ is methyl.
21. The compound of claim 20 wherein Z is fluorine, chlorine, bromine, iodine, cyano, nitro, amino, alkoxy-carbonylamino of 1 to 6 alkyl carbon atoms, di(alkyl-carbonyl)amino in which each alkyl is of 1 to 6 carbon atoms, or hydroxysulfonyl.
22. The compound of claim 20 wherein Z is -QR.
- 25 23. The compound of claim 22 wherein Q is NR⁷.
24. The compound of claim 23 wherein R⁷ is hydrogen.
25. The compound of claim 24 wherein R is alkyl of 1 to 4 carbon atoms, cycloalkyl of 5 or 6 carbon atoms, 2-propenyl, or 2-propynyl.
- 30
26. The compound of claim 22 wherein Q is oxygen or sulfur.
- 35 27. The compound of claim 26 wherein R is alkyl of 1 to 4 carbon atoms, cycloalkyl of 5 or 6 carbon atoms,

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alkoxyalkyl of 2 to 4 carbon atoms, alkoxyalkoxyalkyl of 3 to 5 carbon atoms, alkylthioalkyl of 2 to 4 carbon atoms, alkylsulfinylalkyl of 2 to 4 carbon atoms, alkylsulfonylalkyl of 2 to 4 carbon atoms, trimethyl-
5 silyl(alkyl of 1 to 4 carbon atoms), alkenyl or alkynyl of 3 to 5 carbon atoms, fluoroalkyl of 1 to 3 carbon atoms, cyanoalkyl of 1 to 3 alkyl carbon atoms, halo-alkenyl or haloalkynyl of 3 to 5 carbon atoms, alkyl-
10 carbonyl of 1 to 4 alkyl carbon atoms, or dialkylamino-
carbonyl or dialkylaminothiocarbonyl in which each
alkyl is of 1 to 4 carbon atoms.

28. The compound of claim 27 wherein Q is oxygen and R is alkyl of 1 to 4 carbon atoms, alkoxyalkyl of 2 to 4 carbon atoms, cyanoalkyl of 1 to 3 alkyl carbon atoms, or alkynyl or haloalkynyl of 3 to 5 carbon atoms.
15

29. The compound of claim 28 wherein R is 1-methyl-ethyl, methoxymethyl, cyanomethyl, 2-propynyl,
20 3-bromo-2-propynyl, or 3-iodo-2-propynyl.

30. The compound of claim 29 wherein R is methoxy-methyl or 2-propynyl.

25 31. The compound of claim 20 wherein Z is -CO-R⁶.

32. The compound of claim 31 wherein R⁶ is hydroxy, alkoxy or alkylthio of 1 to 4 carbon atoms, alkoxy-alkoxy of 2 to 4 carbon atoms, amino, or alkylamino or
30 dialkylamino in which each alkyl independently is unsubstituted or substituted with alkoxy of 1 to 4 carbon atoms.

33. The compound of claim 20 wherein Z is -S(O)_mR⁸.
35

34. The compound of claim 33 wherein m is 1 or 2 and R⁸ is alkyl of 1 to 4 carbon atoms or alkenyl or

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alkynyl of 3 to 5 carbon atoms.

35. The compound of claim 20 wherein Z is $-Q^2R^9$.
- 5 36. The compound of claim 35 wherein R⁹ is selected from the group consisting of 1-methyl-3-pyrrolidinyl, furfuryl, 2-thienylmethyl, 3-tetrahydrofuranyl, tetrahydrofurfuryl, tetrahydropyran-2-ylmethyl, 1,3-dioxolan-2-ylmethyl, 2-(1,3-dioxolan-2-yl)ethyl, 2,2-dimethyl-1,3-dioxolan-4-ylmethyl, 3-(2-methyl-1,3-dioxolan-2-yl)propyl, 1,3-dioxan-4-ylmethyl, 1,4-benzodioxan-2-ylmethyl, tetrahydro-4H-pyran-4-yl, 5,6-dihydro-2H-pyran-3-ylmethyl, 2,2-dimethyl-1,3-dithiolan-4-ylmethyl, tetrahydro-4H-thiopyran-4-yl, tetrahydrothien-3-yl, 1-oxotetrahydrothien-3-yl, 1,1-dioxotetrahydrothien-3-yl, 2,2-dimethyl-1,1,3,3-tetraoxo-1,3-dithiolan-4-ylmethyl, 1,1-dioxotetrahydro-4H-thiopyran-4-yl, and 1,3-oxothiolan-2-ylmethyl.
- 20 37. The compound of claim 36 wherein Q² is oxygen.
38. The compound of claim 20 wherein Z is $-OSO_2R^{10}$.
- 25 39. The compound of claim 38 wherein R¹⁰ is selected from phenyl, methyl, ethyl, propyl, butyl, 1-methyl-ethyl, 1-methylpropyl, 2-methylpropyl, 3-methylbutyl, chloromethyl, 3-chloropropyl, trifluoromethyl, cyano-methyl, methylamino, dimethylamino, dimethylaminoethyl, 2-methoxyethyl, and 2-ethoxyethyl.
- 30 40. The compound of claim 20 wherein Z is $-NHN=C(R^{11})(R^{12})$.
41. The compound of claim 20 wherein Z is $-Q-CR^3R^4-CO-Q^1-R^5$.
- 35 42. The compound of claim 41 wherein R³ is hydrogen or methyl and R⁴ is hydrogen, methyl, methoxy, or

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ethoxy.

43. The compound of claim 42 wherein R³ is hydrogen and R⁴ is hydrogen or methyl.

5

44. The compound of claim 43 wherein Q is O, S, or NH.

10 45. The compound of claim 44 wherein Z is -NHCH₂CO₂R⁵ or -NHCH(CH₃)CO₂R⁵ and R⁵ is alkyl of 1 to 6 carbon atoms, cycloalkylmethyl of 3 to 7 ring carbon atoms, cycloalkyl of 3 to 7 carbon atoms, haloalkyl of 1 to 5 carbon atoms, alkoxyalkyl of 2 to 6 carbon atoms, or cyanoalkyl of 1 to 5 alkyl carbon atoms.

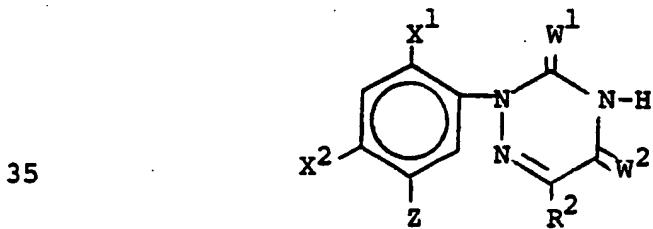
15 46. The compound of claim 45 wherein Z is -NHCH(CH₃)CO₂R⁵ and R⁵ is alkyl of 1 to 4 carbon atoms.

20 47. The compound of claim 44 wherein Z is -OCH(CH₃)-CO-Q¹-R⁵ and Q¹ and R⁵ together represent a phenylsulfonylamino group in which the phenyl is unsubstituted or substituted with fluorine, chlorine, bromine, alkyl of 1 to 4 carbon atoms, alkoxy of 1 to 4 carbon atoms, or alkoxycarbonyl of 1 to 4 alkyl carbon atoms.

25

48. The compound of claim 47 wherein the phenyl moiety of the phenylsulfonylamino group is substituted with chlorine.

30 49. A compound of the formula



wherein W^1 and W^2 are independently oxygen or sulfur;

R^2 is hydrogen, hydroxycarbonyl, or methyl;

X^1 is fluorine;

5 X^2 is chlorine or bromine;

Z is fluorine, chlorine, bromine, iodine, cyano, nitro, amino, alkoxy carbonylamino of 1 to 6 alkyl carbon atoms, di(alkylcarbonyl)amino in which each alkyl is of 1 to 6 carbon atoms, hydroxysulfonyl,

10 halosulfonyl, alkyl of 1 to 6 carbon atoms, haloalkyl of 1 to 5 carbon atoms, $-QR$, $-CO-R^6$, $-S(O)R^8$, $-Q^2R^9$, $-OSO_2R^{10}$, $-NHN=CR^{11}R^{12}$, or $-Q-CR^3R^4-CO-Q^1-R^5$;

Q and Q^1 are independently O, S, or NR^7 in which R^7 is hydrogen or alkyl of 1 to 6 carbon atoms;

15 Q^2 is O or S;

R is hydrogen, alkyl of 1 to 6 carbon atoms (which is unsubstituted or substituted with cycloalkyl of 3 to 7 carbon atoms), cycloalkyl of 3 to 7 carbon atoms (which is unsubstituted or substituted with alkyl of 1 to 6 carbon atoms), benzyl, alkoxyalkyl of 2 to 8 carbon atoms, alkoxyalkoxyalkyl of 3 to 8 carbon atoms, alkylthioalkyl, alkylsulfinylalkyl, or alkylsulfonylalkyl of 2 to 8 carbon atoms, tri(alkyl of 1 to 4 carbon atoms)silyl(alkyl of 1 to 4 carbon atoms), 25 cyanoalkyl of 1 to 5 alkyl carbon atoms, alkenyl or haloalkenyl of 2 to 5 carbon atoms, alkynyl or haloalkynyl of 2 to 5 carbon atoms, haloalkyl of 1 to 5 carbon atoms, alkylcarbonyl of 1 to 6 alkyl carbon atoms, or dialkylaminocarbonyl or dialkylaminothiocarbonyl in which each alkyl is of 1 to 6 carbon atoms;

30 R^3 is hydrogen or alkyl of 1 to 4 carbon atoms,

and R^4 is hydrogen, alkyl of 1 to 4 carbon atoms, or alkoxy of 1 to 4 carbon atoms;

R^5 is hydrogen, alkyl of 1 to 6 carbon atoms

35 (which is unsubstituted or substituted with cycloalkyl of 3 to 7 carbon atoms), cycloalkyl of 3 to 7 carbon atoms (which is unsubstituted or substituted with alkyl

of 1 to 4 carbon atoms), alkoxyalkyl or alkylthioalkyl of 2 to 6 carbon atoms, haloalkyl of 1 to 5 carbon atoms, alkenyl of 2 to 5 carbon atoms, cycloalkenyl of 5 to 7 carbon atoms (which is unsubstituted or substituted with alkyl of 1 to 4 carbon atoms), cycloalkenyl-alkyl of 6 to 10 carbon atoms, phenyl or phenylmethyl (each of which is unsubstituted or ring-substituted with fluorine, chlorine, bromine, or alkyl, alkoxy or alkylthio of 1 to 4 carbon atoms), cyanoalkyl of 1 to 5 alkyl carbon atoms, alkynyl of 2 to 5 carbon atoms, alkylimino of 1 to 6 carbon atoms (which is unsubstituted or substituted with cycloalkyl of 3 to 7 carbon atoms), or cycloalkylimino of 5 to 7 carbon atoms (which is unsubstituted or substituted with alkyl of 1 to 4 carbon atoms); or Q¹ and R⁵ together represent a phenylsulfonylamino group in which the phenyl is unsubstituted or substituted with fluorine, chlorine, bromine, alkyl of 1 to 4 carbon atoms, alkoxy of 1 to 4 carbon atoms, or alkoxycarbonyl of 1 to 4 alkyl carbon atoms;

R⁶ is hydroxy, alkoxy or alkylthio of 1 to 6 carbon atoms, alkoxyalkoxy of 2 to 6 carbon atoms, amino, or alkylamino or dialkylamino wherein each alkyl is of 1 to 6 carbon atoms and is unsubstituted or substituted with alkoxy of 1 to 4 carbon atoms;

R⁸ is alkyl of 1 to 6 carbon atoms or alkenyl or alkynyl of 2 to 5 carbon atoms, and m is 1 or 2;

R⁹ is a 5- or 6-membered ring heterocyclic group of 1 or 2 same or different heteroatoms selected from O, S, and N or an alkyl radical of 1 to 5 carbon atoms substituted with said heterocyclic group;

R¹⁰ is alkyl of 1 to 6 carbon atoms (which is unsubstituted or substituted with halogen, cyano, alkoxy or alkylthio of 1 to 4 carbon atoms, or alkyl-amino or dialkylamino in which alkyl is of 1 to 4 carbon atoms), phenyl, or alkylamino or dialkylamino in which alkyl is of 1 to 4 carbon atoms; and

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R^{11} is hydrogen or alkyl of 1 to 4 carbon atoms and R^{12} is alkyl of 1 to 4 carbon atoms, or $C(R^{11})(R^{12})$ taken as a unit is cycloalkyl of 3 to 7 carbon atoms.

5

50. The compound of claim 49 wherein R^2 is hydrogen and W^1 and W^2 are both oxygen.

51. The compound of claim 50 wherein Z is fluorine, chlorine, bromine, iodine, cyano, nitro, amino, hydroxysulfonyl, chlorosulfonyl, or a group -OR in which R is alkyl of 1 to 6 carbon atoms, benzyl, alkoxyalkyl of 2 to 4 carbon atoms, or alkenyl or alkynyl of 2 to 5 carbon atoms.

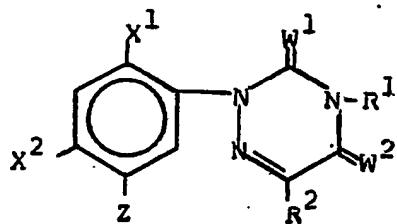
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52. The compound of claim 51 wherein Z is cyano, nitro, or the group -OR.

53. The compound of claim 52 wherein Z is the group -OR and R is alkyl of 1 to 4 carbon atoms.

54. A compound of the formula

25



30 wherein W^1 and W^2 are independently oxygen or sulfur; R^1 is alkyl of 1 to 6 carbon atoms, haloalkyl of 1 to 5 carbon atoms, cyanoalkyl of 1 to 5 alkyl carbon atoms, alkenyl or alkynyl of 2 to 5 carbon atoms or alkoxyalkyl, alkylthioalkyl, alkylsulfinylalkyl, or
35 alkylsulfonylalkyl of 2 to 5 carbon atoms; R^2 is hydrogen or alkyl of 1 to 4 carbon atoms; X^1 is fluorine or chlorine; X^2 is chlorine or bromine; and

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Z is -OH, -SH, or NH₂.

55. The compound of claim 54 wherein Z is -NH₂, W¹ and W² are both oxygen, R¹ is methyl, R² is
5 hydrogen, and X¹ is fluorine.

56. The compound of claim 54 wherein Z is -OH or -SH.

57. The compound of claim 56 wherein Z is -SH, W¹
10 and W² are both oxygen, R¹ is methyl, R² is
hydrogen, and X¹ is fluorine.

58. The compound of claim 56 wherein Z is -OH.

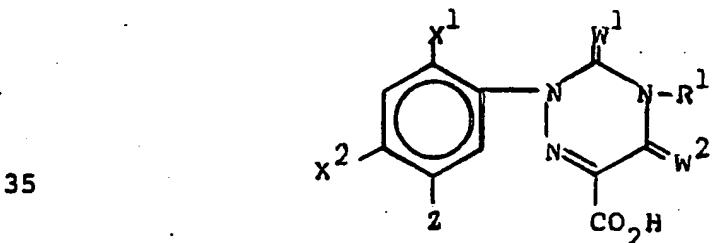
15 59. The compound of claim 58 wherein R² is hydrogen.

60. The compound of claim 59 wherein R¹ is alkyl of
1 to 4 carbon atoms, cyanoalkyl of 1 to 3 alkyl carbon
atoms, fluoroalkyl of 1 to 3 carbon atoms, alkenyl or
20 alkynyl of 3 to 5 carbon atoms, alkoxyalkyl of 2 to 4
carbon atoms, alkylthioalkyl of 2 to 4 carbon atoms,
alkylsulfinylalkyl of 2 to 4 carbon atoms, or alkyl-
sulfonylalkyl of 2 to 4 carbon atoms.

25 61. The compound of claim 60 wherein R¹ is methyl.

62. The compound of claim 61 wherein W¹ and W² are
both oxygen and X¹ is fluorine.

30 63. A compound of the formula



wherein W^1 and W^2 are independently oxygen or sulfur;

R^1 is alkyl of 1 to 6 carbon atoms, haloalkyl of 1 to 5 carbon atoms, cyanoalkyl of 1 to 5 alkyl carbon atoms, alkenyl or alkynyl of 2 to 5 carbon atoms, or alkoxyalkyl, alkylthioalkyl, alkylsulfinylalkyl, or alkylsulfonylalkyl of 2 to 5 carbon atoms,

X^1 is fluorine;

X^2 is chlorine or bromine;

Z is fluorine, chlorine, bromine, iodine, cyano, nitro, amino, alkoxy carbonyl amino of 1 to 6 alkyl carbon atoms, di(alkylcarbonyl)amino in which each alkyl is of 1 to 6 carbon atoms, hydroxysulfonyl, halosulfonyl, alkyl of 1 to 6 carbon atoms, haloalkyl of 1 to 5 carbon atoms, $-QR$, $-CO-R^6$, $-S(O)_{m}R^8$, $-Q^2R^9$, $-OSO_2R^{10}$, $-NHN=CR^{11}R^{12}$, or $-Q-CR^3R^4-CO-Q^1-R^5$;

Q and Q^1 are independently O, S, or NR⁷ in which R⁷ is hydrogen or alkyl of 1 to 6 carbon atoms;

Q^2 is O or S;

R is hydrogen, alkyl of 1 to 6 carbon atoms (which is unsubstituted or substituted with cycloalkyl of 3 to 7 carbon atoms), cycloalkyl of 3 to 7 carbon atoms (which is unsubstituted or substituted with alkyl of 1 to 6 carbon atoms), benzyl, alkoxyalkyl of 2 to 8 carbon atoms, alkoxyalkoxyalkyl of 3 to 8 carbon atoms,

alkylthioalkyl, alkylsulfinylalkyl, or alkylsulfonylalkyl of 2 to 8 carbon atoms, tri(alkyl of 1 to 4 carbon atoms)silyl(alkyl of 1 to 4 carbon atoms), cyanoalkyl of 1 to 5 alkyl carbon atoms, alkenyl or haloalkenyl of 2 to 5 carbon atoms, alkynyl or haloalkynyl of 2 to 5 carbon atoms, haloalkyl of 1 to 5 carbon atoms, alkylcarbonyl of 1 to 6 alkyl carbon atoms, or dialkylaminocarbonyl or dialkylaminothiocarbonyl in which each alkyl is of 1 to 6 carbon atoms;

R^3 is hydrogen or alkyl of 1 to 4 carbon atoms, and R^4 is hydrogen, alkyl of 1 to 4 carbon atoms, or alkoxy of 1 to 4 carbon atoms;

R^5 is hydrogen, alkyl of 1 to 6 carbon atoms (which is unsubstituted or substituted with cycloalkyl of 3 to 7 carbon atoms), cycloalkyl of 3 to 7 carbon atoms (which is unsubstituted or substituted with alkyl of 1 to 4 carbon atoms), alkoxyalkyl or alkylthioalkyl of 2 to 6 carbon atoms, haloalkyl of 1 to 5 carbon atoms, alkenyl of 2 to 5 carbon atoms, cycloalkenyl of 5 to 7 carbon atoms (which is unsubstituted or substituted with alkyl of 1 to 4 carbon atoms), cycloalkenyl-alkyl of 6 to 10 carbon atoms, phenyl or phenylmethyl (each of which is unsubstituted or ring-substituted with fluorine, chlorine, bromine, or alkyl, alkoxy or alkylthio of 1 to 4 carbon atoms), cyanoalkyl of 1 to 5 alkyl carbon atoms, alkynyl of 2 to 5 carbon atoms,

15 alkylimino of 1 to 6 carbon atoms (which is unsubstituted or substituted with cycloalkyl of 3 to 7 carbon atoms), or cycloalkylimino of 5 to 7 carbon atoms (which is unsubstituted or substituted with alkyl of 1 to 4 carbon atoms); or Q^1 and R^5 together represent

20 a phenylsulfonylamino group in which the phenyl is unsubstituted or substituted with fluorine, chlorine, bromine, alkyl of 1 to 4 carbon atoms, alkoxy of 1 to 4 carbon atoms, or alkoxycarbonyl of 1 to 4 alkyl carbon atoms;

25 R^6 is hydroxy, alkoxy or alkylthio of 1 to 6 carbon atoms, alkoxyalkoxy of 2 to 6 carbon atoms, amino, or alkylamino or dialkylamino wherein each alkyl is of 1 to 6 carbon atoms and is unsubstituted or substituted with alkoxy of 1 to 4 carbon atoms;

30 R^8 is alkyl of 1 to 6 carbon atoms or alkenyl or alkynyl of 2 to 5 carbon atoms, and m is 1 or 2; R^9 is a 5- or 6-membered ring heterocyclic group of 1 or 2 same or different heteroatoms selected from O, S, and N or an alkyl radical of 1 to 5 carbon atoms

35 substituted with said heterocyclic group;

R^{10} is alkyl of 1 to 6 carbon atoms (which is unsubstituted or substituted with halogen, cyano,

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alkoxy or alkylthio of 1 to 4 carbon atoms, or alkyl-amino or dialkylamino in which alkyl is of 1 to 4 carbon atoms), phenyl, or alkylamino or dialkylamino in which alkyl is of 1 to 4 carbon atoms; and

5 R¹¹ is hydrogen or alkyl of 1 to 4 carbon atoms and R¹² is alkyl of 1 to 4 carbon atoms, or C(R¹¹)(R¹²) taken as a unit is cycloalkyl of 3 to 7 carbon atoms.

64. The compound of claim 63 wherein Z is fluorine,
10 chlorine, bromine, iodine, cyano, nitro, amino,
hydroxysulfonyl, chlorosulfonyl, or a group -OR in
which R is alkyl of 1 to 6 carbon atoms, benzyl,
alkoxyalkyl of 2 to 4 carbon atoms, or alkenyl or
alkynyl of 2 to 5 carbon atoms.

15 65. The compound of claim 64 wherein R¹ is alkyl of
1 to 4 carbon atoms, cyanoalkyl of 1 to 3 alkyl carbon
atoms, fluoroalkyl of 1 to 3 carbon atoms, alkenyl or
alkynyl of 3 to 5 carbon atoms, alkoxyalkyl of 2 to 4
20 carbon atoms, alkylthioalkyl of 2 to 4 carbon atoms,
alkylsulfinylalkyl of 2 to 4 carbon atoms; or
alkylsulfonylalkyl of 2 to 4 carbon atoms.

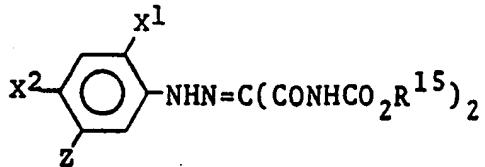
66. The compound of claim 65 wherein R¹ is methyl.
25 67. The compound of claim 66 wherein W¹ and W² are
both oxygen.

68. The compound of claim 67 wherein Z is cyano,
30 nitro, or the group -OR.

69. The compound of claim 68 wherein Z is the group
-OR and R is alkyl of 1 to 4 carbon atoms.

70. The compound of the formula

5



wherein R^{15} is an alkyl group which is unsubstituted or substituted;

X^1 is fluorine;

10 X^2 is chlorine or bromine;

Z is fluorine, chlorine, bromine, iodine, cyano, nitro, amino, alkoxy carbonyl amino of 1 to 6 alkyl carbon atoms, di(alkyl carbonyl) amino in which each alkyl is of 1 to 6 carbon atoms, hydroxysulfonyl, halo-15 sulfonyl, alkyl of 1 to 6 carbon atoms, haloalkyl of 1 to 5 carbon atoms, $-QR$, $-CO-R^6$, $-S(O)_mR^8$, $-Q^2R^9$, $-OSO_2R^{10}$, $-NHN=CR^{11}R^{12}$, or $-Q-CR^3R^4-CO-Q^1-R^5$;

Q and Q^1 are independently 0, S, or NR^7 in which R^7 is hydrogen or alkyl of 1 to 6 carbon atoms;

20 Q^2 is 0 or S;

R is hydrogen, alkyl of 1 to 6 carbon atoms (which is unsubstituted or substituted with cycloalkyl of 3 to 7 carbon atoms), cycloalkyl of 3 to 7 carbon atoms (which is unsubstituted or substituted with alkyl of 1 to 6 carbon atoms), benzyl, alkoxyalkyl of 2 to 8 carbon atoms, alkoxyalkoxyalkyl of 3 to 8 carbon atoms, alkylthioalkyl, alkylsulfinylalkyl, or alkylsulfonylalkyl of 2 to 8 carbon atoms, tri(alkyl of 1 to 4 carbon atoms)silyl(alkyl of 1 to 4 carbon atoms),

30 cyanoalkyl of 1 to 5 alkyl carbon atoms, alkenyl or haloalkenyl of 2 to 5 carbon atoms, alkynyl or haloalkynyl of 2 to 5 carbon atoms, haloalkyl of 1 to 5 carbon atoms, alkylcarbonyl of 1 to 6 alkyl carbon atoms, or dialkylaminocarbonyl or dialkylaminothiocarbonyl in which each alkyl is of 1 to 6 carbon atoms;

35 R^3 is hydrogen or alkyl of 1 to 4 carbon atoms, and R^4 is hydrogen, alkyl of 1 to 4 carbon atoms, or

alkoxy of 1 to 4 carbon atoms;

- R⁵ is hydrogen, alkyl of 1 to 6 carbon atoms (which is unsubstituted or substituted with cycloalkyl of 3 to 7 carbon atoms), cycloalkyl of 3 to 7 carbon atoms (which is unsubstituted or substituted with alkyl of 1 to 4 carbon atoms), alkoxyalkyl or alkylthioalkyl of 2 to 6 carbon atoms, haloalkyl of 1 to 5 carbon atoms, alkenyl of 2 to 5 carbon atoms, cycloalkenyl of 5 to 7 carbon atoms (which is unsubstituted or substituted with alkyl of 1 to 4 carbon atoms), cycloalkenyl-
5 alkyl of 6 to 10 carbon atoms, phenyl or phenylmethyl (each of which is unsubstituted or ring-substituted with fluorine, chlorine, bromine, or alkyl, alkoxy or alkylthio of 1 to 4 carbon atoms), cyanoalkyl of 1 to 5 alkyl carbon atoms, alkynyl of 2 to 5 carbon atoms,
10 alkylimino of 1 to 6 carbon atoms (which is unsubstituted or substituted with cycloalkyl of 3 to 7 carbon atoms), or cycloalkylimino of 5 to 7 carbon atoms (which is unsubstituted or substituted with alkyl of 1 to 4 carbon atoms); or Q¹ and R⁵ together represent
15 a phenylsulfonylamino group in which the phenyl is unsubstituted or substituted with fluorine, chlorine, bromine, alkyl of 1 to 4 carbon atoms, alkoxy of 1 to 4 carbon atoms, or alkoxycarbonyl of 1 to 4 alkyl carbon atoms;
20 R⁶ is hydroxy, alkoxy or alkylthio of 1 to 6 carbon atoms, alkoxyalkoxy of 2 to 6 carbon atoms, amino, or alkylamino or dialkylamino wherein each alkyl is of 1 to 6 carbon atoms and is unsubstituted or substituted with alkoxy of 1 to 4 carbon atoms;
25 R⁸ is alkyl of 1 to 6 carbon atoms or alkenyl or alkynyl of 2 to 5 carbon atoms, and m is 1 or 2;
30 R⁹ is a 5- or 6-membered ring heterocyclic group of 1 or 2 same or different heteroatoms selected from O, S, and N or an alkyl radical of 1 to 5 carbon atoms
35 substituted with said heterocyclic group;
R¹⁰ is alkyl of 1 to 6 carbon atoms (which is

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unsubstituted or substituted with halogen, cyano, alkoxy or alkylthio of 1 to 4 carbon atoms, or alkyl-amino or dialkylamino in which alkyl is of 1 to 4 carbon atoms), phenyl, or alkylamino or dialkylamino in 5 which alkyl is of 1 to 4 carbon atoms; and

R¹¹ is hydrogen or alkyl of 1 to 4 carbon atoms and R¹² is alkyl of 1 to 4 carbon atoms, or C(R¹¹)(R¹²) taken as a unit is cycloalkyl of 3 to 7 carbon atoms.

10 71. The compound of claim 70 wherein R¹⁵ is alkyl of 1 to 4 carbon atoms and Z is fluorine, chlorine, bromine, iodine, cyano, nitro, amino, hydroxysulfonyl, chlorosulfonyl, or a group -OR in which R is alkyl of 1 to 6 carbon atoms, benzyl, alkoxyalkyl of 2 to 4 carbon 15 atoms, or alkenyl or alkynyl of 2 to 5 carbon atoms.

72. The compound of claim 71 wherein Z is cyano, nitro, or the group -OR.

20 73. The compound of claim 72 wherein Z is the group -OR and R is alkyl of 1 to 4 carbon atoms.

74. An herbicidal composition comprising an herbicidally effective amount of a compound of claim 8 in 25 admixture with a carrier suitable for the intended herbicidal use.

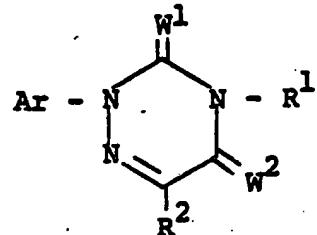
75. A method for controlling undesired plant growth, which comprises applying to the locus where control is desired an herbicidally effective amount of the composition of claim 74.

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76. A process for controlling undesired plant growth characterized by applying to the locus where control is desired an herbicidally effective amount of an herbicidal compound of the formula

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where Ar is a dihalophenyl radical; W¹ and W² are independently selected from oxygen and sulfur; R¹ is alkyl of 1 to 6 carbon atoms, cyanoalkyl of 1 to 5 carbon atoms, haloalkyl of 1 to 5 carbon atoms, alkenyl or alkynyl of 2 to 5 carbon atoms, alkoxyalkyl, alkylthioalkyl, alkylsulfinylalkyl, or alkylsulfonylalkyl of 2 to 5 carbon atoms, or amino; and R² is hydrogen, alkyl of 1 to 4 carbon atoms, haloalkyl of 1 to 4 carbon atoms, alkenyl or alkynyl of 2 to 4 carbon atoms, alkoxyalkyl of 2 to 4 carbon atoms, amino, fluorine, chlorine, bromine, hydroxycarbonyl, or alkoxy carbonyl of 1 to 4 alkyl carbon atoms in admixture with a carrier suitable for the intended herbicidal use.

77. The process of claim 76 characterized in that the dihalophenyl radical is a 2,4-dihalophenyl radical.

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78. The process of claim 77 characterized in that R¹ is methyl, fluoromethyl, or cyanomethyl and R² is hydrogen.

35 79. The process of claim 78 characterized in that the

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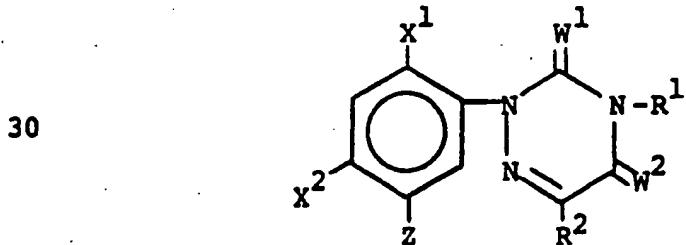
2,4-dihalophenyl radical is a 5-(alkoxy of 1 to 6 carbon atoms)-2,4-dihalophenyl radical.

80. The process of claim 78 characterized in that the
5 2,4-dihalophenyl radical is a 5-(alkynyoxy of 2 to 5 carbon atoms)-2,4-dihalophenyl radical.

81. The process of claim 78 characterized in that the
2,4-dihalophenyl radical is a 5-(alkoxyalkoxy of 2 to 8
10 carbon atoms)-2,4-dihalophenyl radical.

82. The process of claim 78 characterized in that the
2,4-dihalophenyl radical is substituted at the C-5 position with a group of the formula -Q-CH₂(CH₃)-CO-Q¹-R⁵
15 in which Q and Q¹ are independently O, S, or NH and R⁵ is alkyl of 1 to 6 carbon atoms, or Q¹ and R⁵ together form a phenylsulfonylamino group in which the phenyl is unsubstituted or substituted with fluorine, chlorine, bromine, alkyl of 1 to 4 carbon atoms, alkoxy of 1 to 4
20 carbon atoms, or alkoxycarbonyl of 1 to 4 alkyl carbon atoms.

83. A process for controlling undesired plant growth characterized by applying to the locus where control is
25 desired an herbicidally effective amount of an herbicidal compound of the formula



35 wherein W¹ and W² are independently oxygen or sulfur;

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R¹ is alkyl of 1 to 6 carbon atoms, haloalkyl of 1 to 5 carbon atoms, cyanoalkyl of 1 to 5 alkyl carbon atoms, alkenyl or alkynyl of 2 to 5 carbon atoms, alkoxyalkyl, alkylthioalkyl or 2 to 5 carbon atoms, or

5 amino;

R² is hydrogen or alkyl of 1 to 4 carbon atoms;

X¹ is fluorine or chlorine;

X² is fluorine, chlorine, bromine, alkyl of 1 to 6 carbon atoms, haloalkyl of 1 to 5 carbon atoms, or 10 alkoxy of 1 to 6 carbon atoms;

Z is hydrogen, fluorine, chlorine, bromine, iodine, cyano, nitro, amino, alkoxy carbonyl amino of 1 to 6 alkyl carbon atoms, di(alkylcarbonyl)amino in which each alkyl is of 1 to 6 carbon atoms, hydroxysulfonyl, 15 alkyl of 1 to 6 carbon atoms, haloalkyl of 1 to 5 carbon atoms, -QR, -CO-R⁶, -S(O)_mR⁸, -Q²R⁹, -OSO₂R¹⁰, NHN=CR¹¹R¹², or -Q-CR³R⁴-CO-Q-R⁵;

Q and Q¹ are independently O, S, or NR⁷ in which R⁷ is hydrogen or alkyl of 1 to 6 carbon atoms;

20 Q² is O or S;

R is hydrogen, alkyl of 1 to 6 carbon atoms (which is unsubstituted or substituted with cycloalkyl of 3 to 7 carbon atoms), cycloalkyl of 3 to 7 carbon atoms (which is unsubstituted or substituted with alkyl of 1 to 6 carbon atoms), alkoxyalkyl of 2 to 8 carbon atoms, 25 alkoxyalkoxyalkyl of 3 to 8 carbon atoms, alkylthioalkyl, alkylsulfinylalkyl, or alkylsulfonylalkyl of 2 to 8 carbon atoms, tri(alkyl of 1 to 4 carbon atoms)-silyl(alkyl of 1 to 4 carbon atoms), cyanoalkyl of 1 to 30 5 alkyl carbon atoms, alkenyl or haloalkenyl of 2 to 5 carbon atoms, alkynyl or haloalkynyl of 2 to 5 carbon atoms, haloalkyl of 1 to 5 carbon atoms, alkylcarbonyl of 1 to 6 alkyl carbon atoms, or dialkylaminocarbonyl or dialkylaminothiocarbonyl in which each alkyl is of 1 to 35 6 carbon atoms;

R³ is hydrogen or alkyl of 1 to 4 carbon atoms,

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and R⁴ is hydrogen, alkyl of 1 to 4 carbon atoms, or alkoxy of 1 to 4 carbon atoms;

R⁵ is hydrogen, alkyl of 1 to 6 carbon atoms (which is unsubstituted or substituted with cycloalkyl of 3 to 7 carbon atoms), cycloalkyl of 3 to 7 carbon atoms (which is unsubstituted or substituted with alkyl of 1 to 4 carbon atoms), alkoxyalkyl or alkylthioalkyl of 2 to 6 carbon atoms, haloalkyl of 1 to 5 carbon atoms, alkenyl of 2 to 5 carbon atoms, cycloalkenyl of 5 to 7 carbon atoms (which is unsubstituted or substituted with alkyl of 1 to 4 carbon atoms), cycloalkenyl-alkyl of 6 to 10 carbon atoms, phenyl or phenylmethyl (each of which is unsubstituted or ring-substituted with fluorine, chlorine, bromine, or alkyl, alkoxy or alkylthio of 1 to 4 carbon atoms), cyanoalkyl of 1 to 5 alkyl carbon atoms, alkynyl of 2 to 5 carbon atoms, alkylimino of 1 to 6 carbon atoms (which is unsubstituted or substituted with cycloalkyl of 3 to 7 carbon atoms), or cycloalkylimino of 5 to 7 carbon atoms

20 (which is unsubstituted or substituted with alkyl of 1 to 4 carbon atoms); or Q¹ and R⁵ together represent a phenylsulfonylamino group in which the phenyl is unsubstituted or substituted with fluorine, chlorine, bromine, alkyl of 1 to 4 carbon atoms, alkoxy of 1 to 4 carbon atoms, or alkoxy carbonyl of 1 to 4 alkyl carbon atoms;

R⁶ is hydroxy, alkoxy or alkylthio of 1 to 6 carbon atoms, alkoxyalkoxy of 2 to 6 carbon atoms, amino, or alkylamino or dialkylamino wherein each alkyl is of 1 to 6 carbon atoms and is unsubstituted or substituted with alkoxy of 1 to 4 carbon atoms;

R⁸ is alkyl of 1 to 6 carbon atoms or alkenyl or alkynyl of 2 to 5 carbon atoms, and m is 1 or 2;

R⁹ is a 5- or 6-membered ring heterocyclic group of 1 or 2 same or different heteroatoms selected from O, S, and N or an alkyl radical of 1 to 5 carbon atoms

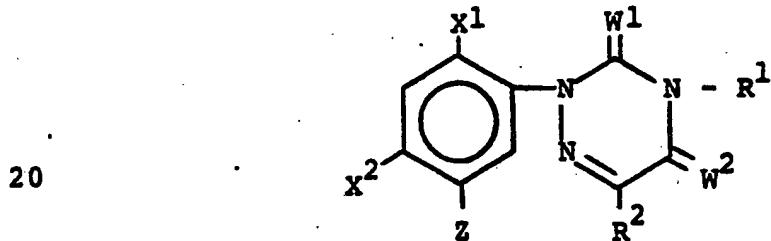
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substituted with said heterocyclic group;

¹⁰ R¹⁰ is alkyl of 1 to 6 carbon atoms (which is unsubstituted or substituted with halogen, cyano, alkoxy or alkylthio of 1 to 4 carbon atoms, or alkyl-
5 amino or dialkylamino in which alkyl is of 1 to 4 carbon atoms), phenyl, or alkylamino or dialkylamino in which alkyl is of 1 to 4 carbon atoms; and

¹¹ R¹¹ is hydrogen or alkyl of 1 to 4 carbon atoms and R¹² is alkyl of 1 to 4 carbon atoms, or C(R¹¹)(R¹²)
10 taken as a unit is cycloalkyl of 3 to 7 carbon atoms; in admixture with a carrier suitable for the intended herbicidal use.

84. A process for producing an herbicidal compound of
15 the formula



wherein W¹ and W² are independently oxygen or
25 sulfur;

R¹ is alkyl of 1 to 6 carbon atoms, haloalkyl of 1 to 5 carbon atoms, cyanoalkyl of 1 to 5 alkyl carbon atoms, alkenyl or alkynyl of 2 to 5 carbon atoms, alkoxyalkyl, alkylthioalkyl, alkylsulfinylalkyl, or
30 alkylsulfonylalkyl of 2 to 5 carbon atoms, or amino;

R² is hydrogen or alkyl of 1 to 4 carbon atoms;

X¹ is fluorine or chlorine;

X² is fluorine, chlorine, bromine, alkyl of 1 to 6 carbon atoms, haloalkyl of 1 to 5 carbon atoms, or
35 alkoxy of 1 to 6 carbon atoms;

Z is hydrogen, fluorine, chlorine, bromine,

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- iodine, cyano, nitro, amino, alkoxy carbonyl amino of 1 to 6 alkyl carbon atoms, di(alkyl carbonyl) amino in which each alkyl is of 1 to 6 carbon atoms, hydroxysulfonyl, alkyl of 1 to 6 carbon atoms,
- 5 haloalkyl of 1 to 5 carbon atoms, -QR, -CO-R⁶, -S(O)_mR⁸, -Q²R⁹, -OSO₂R¹⁰, NHN=CR¹¹R¹², or -Q-CR³R⁴-CO-Q¹-R⁵; Q and Q¹ are independently 0, S, or NR⁷ in which R⁷ is hydrogen or alkyl of 1 to 6 carbon atoms; Q² is 0 or S;
- 10 R is hydrogen, alkyl of 1 to 6 carbon atoms (which is unsubstituted or substituted with cycloalkyl of 3 to 7 carbon atoms), cycloalkyl of 3 to 7 carbon atoms (which is unsubstituted or substituted with alkyl of 1 to 6 carbon atoms), alkoxyalkyl of 2 to 8 carbon atoms,
- 15 alkoxyalkoxyalkyl of 3 to 8 carbon atoms, alkylthio-alkyl, alkylsulfinylalkyl, or alkylsulfonylalkyl of 2 to 8 carbon atoms, tri(alkyl of 1 to 4 carbon atoms)-silyl(alkyl of 1 to 4 carbon atoms), cyanoalkyl of 1 to 5 alkyl carbon atoms, alkenyl or haloalkenyl of 2 to 5 carbon atoms, alkynyl or haloalkynyl of 2 to 5 carbon atoms, haloalkyl of 1 to 5 carbon atoms, alkylcarbonyl of 1 to 6 alkyl carbon atoms, or dialkylaminocarbonyl or dialkylaminothiocarbonyl in which each alkyl is of 1 to 6 carbon atoms;
- 20 25 R³ is hydrogen or alkyl of 1 to 4 carbon atoms, and R⁴ is hydrogen, alkyl of 1 to 4 carbon atoms, or alkoxy of 1 to 4 carbon atoms;
- R⁵ is hydrogen, alkyl of 1 to 6 carbon atoms (which is unsubstituted or substituted with cycloalkyl of 3 to 7 carbon atoms), cycloalkyl of 3 to 7 carbon atoms (which is unsubstituted or substituted with alkyl of 1 to 4 carbon atoms), alkoxyalkyl or alkylthioalkyl of 2 to 6 carbon atoms, haloalkyl of 1 to 5 carbon atoms, alkenyl of 2 to 5 carbon atoms, cycloalkenyl of 5 to 7 carbon atoms (which is unsubstituted or substi-

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tuted with alkyl of 1 to 4 carbon atoms), cycloalkenyl-
alkyl of 6 to 10 carbon atoms, phenyl or phenylmethyl
(each of which is unsubstituted or ring-substituted
with fluorine, chlorine, bromine, or alkyl, alkoxy or
5 alkylthio of 1 to 4 carbon atoms), cyanoalkyl of 1 to 5
alkyl carbon atoms, alkynyl of 2 to 5 carbon atoms,
alkylimino of 1 to 6 carbon atoms (which is unsubsti-
tuted or substituted with cycloalkyl of 3 to 7 carbon
atoms), or cycloalkylimino of 5 to 7 carbon atoms.
10 (which is unsubstituted or substituted with alkyl of 1
to 4 carbon atoms); or Q¹ and R⁵ together represent
a phenylsulfonylamino group in which the phenyl is
unsubstituted or substituted with fluorine, chlorine,
bromine, alkyl of 1 to 4 carbon atoms, alkoxy of 1 to 4
15 carbon atoms, or alkoxycarbonyl of 1 to 4 alkyl carbon
atoms;

R⁶ is hydroxy, alkoxy or alkylthio of 1 to 6
carbon atoms, alkoxyalkoxy of 2 to 6 carbon atoms,
amino, or alkylamino or dialkylamino wherein each alkyl
20 is of 1 to 6 carbon atoms and is unsubstituted or sub-
stituted with alkoxy of 1 to 4 carbon atoms;

R⁸ is alkyl of 1 to 6 carbon atoms or alkenyl or
alkynyl of 2 to 5 carbon atoms, and m is 1 or 2;

R⁹ is a 5- or 6-membered ring heterocyclic group
25 of 1 or 2 same or different heteroatoms selected from
O,S, and N or an alkyl radical of 1 to 5 carbon atoms
substituted with said heterocyclic group;

R¹⁰ is alkyl of 1 to 6 carbon atoms (which is
unsubstituted or substituted with halogen, cyano,
30 alkoxy or alkylthio of 1 to 4 carbon atoms, or alkyl-
amino or dialkylamino in which alkyl is of 1 to 4
carbon atoms), phenyl, or alkylamino or dialkylamino in
which alkyl is of 1 to 4 carbon atoms; and

R¹¹ is hydrogen or alkyl of 1 to 4 carbon atoms
35 and R¹² is alkyl of 1 to 4 carbon atoms, or C(R¹¹)(R¹²)
taken as a unit is cycloalkyl of 3 to 7 carbon atoms;

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characterized by reacting a precursor compound in an appropriate manner to convert it into the herbicidal compound.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US85/01041

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)¹

According to International Patent Classification (IPC) or to both National Classification and IPC Class 560-19 &22
 U.S. Cl. 544/182 71/93 ; Class 560-subs 25,26,13,17,18,
 INT. CL₃ C07 D/253/06; A01N 43/64; C07C 125/073; C07C 79/46

II. FIELDS SEARCHED

Minimum Documentation Searched⁴

Classification System	Classification Symbols
US	544/182; 71/93; 560/25 560/26; 560/9; 560/13/17/18/19/22

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched⁵

**Chemical Abstracts: 1,2,4-triazine
3,5 dione or thione; phenyl hydrazine imine carboacetamide**

III. DOCUMENTS CONSIDERED TO BE RELEVANT¹⁴

Category ⁶	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
A	U.S. A 3,852,289, published 03 December 1974, Mylari et al	
X	U.S. A 3,883,525, published 13 May 1975, Mylari et al	8-69
A	U.S. A 4,058,525 published 15 November 1977, Hofer et al	1-7 and 74-84
X	U.S. A 3,883,527, published 13 May 1975, Brennan	8-69
Y	U.S. A 3,882,115, published 06 May 1975, Mylari	8-69
Y	U.S. A 3,883,528, published 13 May 1975, Mylari	8-69

* Special categories of cited documents:¹⁶

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"g" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search⁹

26 July 1985

Date of Mailing of this International Search Report¹⁰

31 JUL 1985

International Searching Authority¹¹

ISA/US

Signature of Authorized Officer¹²

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

Y

U.S. A 3,912,723, published 14
October 1975, Miller

8-69

V. OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE¹⁰

This International search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. Claim numbers _____ because they relate to subject matter¹¹ not required to be searched by this Authority, namely:

2. Claim numbers _____ because they relate to parts of the International application that do not comply with the prescribed requirements to such an extent that no meaningful International search can be carried out¹², specifically:

VI. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING¹³

This International Searching Authority found multiple inventions in this international application as follows:

(I) Claims 1--69 and 74-84 drawn to triazine ones and thiones

(II) Claims 70--73 drawn in intermediates

1. As all required additional search fees were timely paid by the applicant, this International search report covers all searchable claims of the International application.

2. As only some of the required additional search fees were timely paid by the applicant, this International search report covers only those claims of the International application for which fees were paid, specifically claims:

3. No required additional search fees were timely paid by the applicant. Consequently, this International search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

The additional search fees were accompanied by applicant's protest.

No protest accompanied the payment of additional search fees.